CONTENTS

REVIEW

V. A. Aret
Use of food resources and development of food production technology.................................................. 4

FOOD PRODUCTION TECHNOLOGY

N. I. Gombozhapova, B. A. Bazhenova, S. Yu. Leskova, T. M. Badmaeva, and A. M. Danilov
Influence of the new multicomponent brine on the quality characteristics of the boiled horse meat product................................................................. 11

I. A. Khankhalaeva, I. S. Khamagayaeva, and A. P. Nikiforova
Effects of propionic-acid bacteria and bifidobacteria on the quality of raw smoked sausages................................................................. 20

A. G. Khramtsov, A. V. Blinov, A. A. Blinova, and A. V. Serejav
Influence of the whey type on composition and properties of its mineralizates.......................................... 30

A. N. Ponomarev, E. I. Melnikova, E. V. Bogdanova, and D. V. Kharitonov
Impact of betalactoglobulin hydrolysate on structural and mechanical properties of allergenic potency-restricted yogurt.................................................. 41

Formation and study of symbiotic consortium of lactobacilli to receive a direct application starter............... 51

D. F. Valiulina, N. V. Makarova, and I. A. Kustova
Grape pomace extract and pear in snack production technology............................................................. 63

A. A. Zhuravlev, S. I. Lukina, E. I. Ponomareva, and K. E. Rosiyakova
Optimization of technological parameters of preparation of dough for rusk production.................................................. 73

R. A. Zhuravlev, M. Yu. Tamova, N. A. Bugayets, V. M. Poznyakovskiy, and N. D. Penov
Innovative encapsulation technology of food systems using a by-product of dairy production....................... 81

BIOTECHNOLOGY

A. I. Piskaeva, O. O. Babich, V. F. Dolganyuk, and S. Yu. Garinashov
Analysis of influence of biohumus on the basis of consortium of effective microorganisms on the productivity of winter wheat............................................................. 90

Antibacterial effect of colloidal solutions of silver nanoparticles on microorganisms of cereal crops................................. 100

Determination of the intensity of bacteriocin production by strains of lactic acid bacteria and their effectiveness.................................................. 108

PROCESSES, EQUIPMENT, AND APPARATUS FOR FOOD PRODUCTION

A. V. Batrachenko and N. V. Filimonova
The influence of structural and kinematic parameters of working bodies of the meat grinders on its productivity............................................................. 118

I. A. Evdokimov, S. A. Titov, K. K. Polyansky, and D. S. Saiko
Ultrafiltration concentrating of curd whey after electroflotation treatment.............................................. 131
A. M. Popov, K. B. Plotnikov, and D. V. Donya  
Determination of dependence between thermophysical properties and structural-and-phase characteristics of moist materials  

137

STANDARDIZATION, CERTIFICATION, QUALITY AND SAFETY

Identification of aromatic aldehydes in the express assessment of quality of herbal distilled drinks  

144

Yu. V. Golubtsova  
Physical and chemical indicators and merchandising assessment of wild strawberry, gooseberry, cherry, raspberry, banana, wild rose and kiwi  

154

CHEMISTRY AND ECOLOGY

E. V. Averyanova, M. N. Shkolnikova, and A. V. Frolov  
Dependence of purified rutin quality on activated carbon brand  

165

ECONOMICS

O. V. Glushakova, N. V. Fadeykina, I. V. Baranova, K. Yu. Tsygankov, and V. V. Mikhailov  
Fiscal technologies of budget liquidity management and their role to ensure the sustainable growth of the agrarian sector in the context of global uncertainty  

174

Formation of agro-industrial cluster on the priority social and economic development area of the mono-industry town  

192

E. A. Morozova, E. A. Kranzeeva, and O. P. Kochneva  
Catering service and its quality for university students in municipal formation  

205

INFORMATION

Information for Authors  

216

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REVIEW

USE OF FOOD RESOURCES AND DEVELOPMENT OF FOOD PRODUCTION TECHNOLOGY

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Abstract: Various changes in demographic models of world population and evolution of food production technologies have been considered. Numerical constant values in the hyperbolic model of Heinz’s cybernetics are defined as per the CurveExpert program and based on statistical data of the global population increased for the certain period at the mean square deviation of $S = 74.8$ of one million people a year and the correlation ratio of $r = 0.994$. Note at the same time that the calculated Heinz’s “Doomsday” falls on the 115th year of the life and the date of birth of this model developer. The relation of the world population growth to stages to develop food production technologies has been analyzed. The marginal population is evaluated in terms of the direct energy considerations. A variety of development hypotheses is proposed throughout the human development history based on the Darwin’s model, astrophysics of the solar system and the policy.

Keywords: The von Foerster’s model, the world population, the food technology

INTRODUCTION

This article is aimed to clarify historical, economic and philosophical experience in production and consumption of food and to evaluate prospects for further development in this field of human activity. Currently we face some desperate predictions which make the subject and purpose of our research urgent upon the analysis. For instance, Professor John Beddington [1], UK Government’s scientific adviser, predicted that by 2030 we would face disastrous scarcity of vital resources. By this time, the population will reach 8.3 billion people; the need in energy will jeopardize by 50% where the demand for fresh water will grow by 30%. V.I. Arnold [2], one of the Soviet mathematicians, developed the theory of catastrophes. The mathematical aspect of this poses certain doubts even where such intricate phenomenon as the cataclysm is fully covered addressing the bifurcation theory of differential equations and the theory of smooth reflection peculiarities, though it accentuates the urgency of mathematical analysis of problems, in addition. Ilya Prigogine, the Nobel laureate, in collaboration with Isabelle Stengers [3] looked for methods to restore the union between humans and nature based on new principles to be the solidarity of science, culture and so in addition to the union of humankind and nature.

OBJECTS AND METHODS OF RESEARCH

The research is focused on critical periods in history of technology for food production industry. In 1960, Heinz von Foerster, the scholar [4], published an article in the “Science” Magazine titled “Doomsday. Friday 13, November 2026”. Based on the data on global population growth in 1958 he built a hyperbolic model as per which the world population by 2026 would be unlimited

$$N(t) = \frac{C}{t_0 - t}.$$  

where $N(t)$ is the dependence of the global population on time $t$; $t_0$ is the time constant by Heinz; $C = 199686.86$ is the constant of the global population by demographic data prior to 1950 that we calculated using a mathematic software product. Then the formula (1) takes on the form:

$$N(t) = \frac{199686.86}{2026 - t}.$$  


Fig. 1. Graph plotted on the global population based on statistic data up to 1950 using the CurveExpert software for the empirical formula (2). The standard deviation of the plotted data makes $S = 74.8$ and the correlation coefficient $r$ is equal to 0.994.

RESULTS AND DISCUSSION


However, since 1989 the absolute growth rate of the global population tends to decline (US Census Bureau (USCB), 2008) [6]. By 2100, the growth rate could decline to less than 5 million people a decade. As some demographers limit the growth rate, the modeling will reach 10–12 billion people and some predict on the lower level of the global population stabilization. In this case, for example, the logistic law (Kapitza, 1996 [7]; Verhulst, 1845 [8]; Lotka, 1925 [9]; Volterra, 1926 [10]; Haub, 1995[11]) seems to be more appropriate.

The final scenario of population development is still vague. But it is clear that the Doomsday by Heinz would not occur in 2026 due to the global drive to perpetuity and it may occur for quite different reasons.

The astrophysical concept of the solar system and the Darwinian evolution model basis compile the following arguments on the development of food production technologies.

Photosynthesis is the main source of biological energy, the photosynthetic autotrophs (mainly, the green plants) use solar energy to synthesize organic compounds of inorganic, the heterotrophs (including humans) exist due to energy stored as autotrophic chemical relations. The Sun’s energy resources are not endless. As it radiates, the mass of the Sun is reduced by 4.3 million tons per second (K.–P. Schröder and R. Connor Smith, 2008) [13]. The Sun can generate the energy for photosynthesis on the Earth for about 100 billion years, but the energy required will be “cut off” someday.

Let us consider the process of photosynthesis in detail. There are three stages of photosynthesis: photophysical, photochemical and chemical. At the photophysical stage, the light quanta pigments are absorbed, they transform to the excited state and the energy is transferred to other molecules of the photosystem. At the photochemical stage, the charges separate in the reactive center of the photosynthetic electron transport. The first two stages are jointly called the light-dependent stage of photosynthesis. The third stage takes place with no commitment of the outer world and includes biochemical reactions of organic compound synthesis using the energy stored at the light-dependent stage. Most such reactions as observed in Calvin cycle (J. Bassham, A. Benson, and M. Calvin, 1950) [14] are the processes of gluconeogenesis formation of sugars and starches from carbon dioxide in the air.

In 1941, Melvin Calvin, the American biochemist, proved that the water molecule photolysis is the primary photosynthetic process resulting in oxygen formation released in the atmosphere, and hydrogen used to reduce the carbon dioxide to organic substances. Using the radioactive carbon isotope, 14C, paper chromatography, and conventional methods of the organic chemistry, Calvin and his team managed to trace biosynthetic paths of photochemical processes. By 1956, the pathway of full carbon conversion in the photosynthesis was clarified. In 1961, Calvin was awarded the Nobel Prize in chemistry for researches on carbon dioxide assimilation at plants. The chemical photosynthesis formula may be submitted as follows:

$$6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2.$$  \hfill (3)

Based on such reaction over 1017 kcal of free energy has been stored in the world each year that matches with assimilation over 1010 tons of carbon as carbohydrates and other organic substances (Stayer L., 1985) [15]. If such considerations are deemed correct, the maximum theoretical number of people to be supported by photosynthesis may be calculated at ease. Considering that there are 365 days a year and 1 person needs about 3,000 calories of energy per day, we obtain

$$\frac{10^{17}}{365 \cdot 3000} = 9132420913 \approx 10^{10}. \hfill (4)$$

Apparently, humans and other Earth creatures cannot, for various reasons, use all the stored energy (E.J. Kormondy 1996) [16]. Each link of the trophic chain lost about 90% of useful energy where the mankind still uses reserves of energy as the coal, oil, gas and other energy sources. However, the most
global population fails to receive the adequate quantity and quality of food recently. The food security is the urgent economic challenge for many countries and the global population approaches to photosynthesis energy capacity limits on the planet.

Let us consider the evolutionary classification of food production technologies that justifies the attempts of some forecasts in this area. This technology may be named the first generation technology. The technology of food production was used to be limited to hunting and gathering and differed little from the food production in the animal kingdom. Before humans managed to acquire tools to hunt or farm, insects might have been the important portion of their diet. Cave paintings in the Northern Spain dated back about 30000 to 9000 BC depict the collection of edible insects and wild bee nests suggesting for potential entomophagous society [17].

The Old Stone Age (Lower Paleolithic), that is up to 10–8 thousand BC was the period for the fossil man who used stone, wood and bone tools processed with living employment of thereof to differ significantly from other animals (E. Callaway, 2013 [18]; A.C. Guyton, J.E. Hall, 2006 [19]). The first-generation technology provides the energy to approximately 3 million people. Standing on two legs, the human enjoys more rational way to travel as compared to animals running on four legs. Coupled with the with the human body cooling mechanism by sweating, the human being acquired the ability to catch up any hunting animal at long distances (G.A. Harrison, J.M. Tanner, D.R. Pilbeam, P.T. Baker, 1988) [20]. First-generation technologies represent rudiments of second-generation technology that included the food extraction and transportation, more considerable approaches to power supplies saving, in elements of communal pattern in the hunting and gathering area.

Second-generation technologies may be named as reproduction technologies.

Historically, this technology has evolved around 8–3 thousand BC in the New Stone Age (Neolithic Period). Later on, the human being opened up the skills of grinding and drilling of stone tools, spinning and weaving, pottery art. People hunted together with wolves. They kept domesticated animals – cows, sheep, horses. The hunting transferred to its more intense and adjustable phase. At the same time, the gathering activity was developed to cropping and cultivation of useful plants. This technology provides power to approximately 50 million people by the end of the Neolithic Period and for about 3 billion by the year 1960 (J. Armelagos, 2014) [21]. The increasingly growing needs of human beings are mainly met extensively by increasing the area of existence and the number of livestock. The significance of grain culture should be specifically emphasized where people acquired the skills of massive local cultivation and natural conservation of dried grain.

The importance of the grain crop is evidenced by the well-known expression from the 10th satire of the Roman satirical poet Decimus Junius Juvenal (Decimus Junius Juvenalis in Latin, ab. 60-127) "Bread and circuses"! Juvenal used it to describe the policy of statesmen bribing people with money and food and circus performances. Such acts helped them to seize and hold their power in ancient Rome. (http://antique-lit.niv.ru/antique-lit/gilenson-drevnij- rim/yuvenal.htm) [22].

Ordinary Romans ate mostly cereal products – the bread and porridge. As per the Romans, the hunger meant that the grain, the main food reserves, ended manifested in public disaffection and revolts due to the scarcity of grain or cereal crop failures. The bread was used as the manipulating tool to manage political processes not only in ancient Rome [23].

Currently, there is a wide range of grain and pseudo-seeds food on markets, including the wheat, barley, oats, rye, millet, spelt wheat, green grain and corn. There are such grain crops as kamut, the ancient type of wheat used to be mainly cultivated in ancient Egypt. The American rice is largely marketed to be the pre-cooked, dried and purified wheat coarsely or finely grounded. Valuable pseudo-crops, such as amaranth, Quinoa do not refer to grain crops but to plants of genus wormseed. The buckwheat the grain of which resemble the grain crop refers to plants of the buckwheat family (http://ladychef.ru/ingrediyent/yblei-a-zrelishh-istoriya-i-raznooobrazie-zlakovyh-kultur) [24].

The main cereal crop is the wheat. China is the main wheat producer in the world. In 2014, the share of China in the world grain crop production reached 17.3%, the volume of production made 126.2 million tons. For 10 years, as compared to 2004, the wheat production in China increased by 37.3% or 34.3 million tons. In the next 10 years the growth of wheat production in China is expected to decline in view of the limited land plot available. By 2024, according to the OECD forecast, it will reach 130.9 million tons that almost matches the level of current indexes. According to the USDA, the wheat crop in China by 2024/2025 will reach 133.1 million tons. Among the wheat-producing countries, Russia is ranked third in the world. In 2014, the wheat production in Russia amounted to 59.7 million tons (8.2% of global production). For the 10 consequent years, the figures increased by 31.4% or 16.6 million tons. In 2015, the wheat production in Russia was over 62 million tons as per the Ministry of Agriculture of the Russian Federation making 63.8 million tons (http://ab-centre.ru/page/proizvodstvo-pshenicy-v-mire-strany-proizvoditelii-pshenicy) [25].

The main factor determining the growth of wheat production in the world was an increase in productivity rather than in acreage. The measures aimed to improve the wheat crop technologies and contribute to higher productivity included the increase in the use of mineral fertilizers. In view to increase the yield results and to hold high level of wheat production in the world, we will need to constantly review the mineral fertilizer dosage used. The challenge is to increase the food yields in future by rational use of fertilizer [26].

As it is well-known, the theory of demographic cycles explores the processes of population change under conditions of limited natural resources.
Raymond Pearl [27] proposed this theory and proved that changes in the number of animal populations (and perhaps humans) are described by the so-called logistic curve.

The logistic curve in Fig. 2 shows that the population grows rapidly in the very beginning with the abundance of resources available and high-consumption rate. Then the growth slows down and the population stabilizes near the asymptote corresponding to the maximum possible volume of complete consumption of natural resources.

The achievement of the maximum possible number of population means that there is a minimum level of consumption at the survival margin where the natural increase is completely eliminated by the starvation death. In fact, this state of "hungry homeostasis" turns out to be unstable, the fluctuations in environmental factors result in "demographic catastrophes", catastrophic hunger or epidemic. The disaster causes a drastic reduction in population followed by the new curl in the new demographic cycle recovered [27, 28].

With regard to changes in the population growth rate in graphs 1 and 2, the availability of demographic cycles in history was proved by Wilhelm Abel in the '30s of XX century [29].

Upon the review of data on economic situation in the XII-XIV centuries, V. Abel showed that the population growth fit that period caused the exhaustion of arable land resources; in turn that resulted in food scarcity, increases in grain prices and starvation. Farmers who were unable to get food for their families were forced to cut weekly expenses and went to look for better jobs to larger cities. The urban growth was followed by the craft blooming though the craft itself was not adequate to allow food for the entire surplus population, and the cities were full of unemployed and the poor. Hunger and poverty resulted in riots both in large cities and in villages. In Flanders, such riots were manifested as the social revolution. The French social struggle ended in adoption of absolutism. In the end, the Black Death epidemic that broke under conditions where millions of people were broken by permanent malnutrition resulted in deaths of half the European population. That was the "demographic catastrophe" to end the demographic cycle. Thus, it describes the cycles by R. Pearl that really existed in the past [30].

The second-generation technologies employ elements of the third-generation technology, that is, the technology intensification. The reproduction rate of human beings is rising through breeding more productive animals and growing more efficient plants.

Third-generation technologies may be named as the intensification. The end of the dominance of the second-generation technology can be roughly specified as the middle of the 20th century, when the humankind exhausted all opportunities of extensive growth of food production: the crops suitable for cultivation, the number of animals limited due to the land plot restriction could no longer be increased. It is believed that population will not grow indefinitely and stabilized totaling, as mentioned above, some 10–15 billion people.

Main peculiarities of the third-generation technology, intensification technology, are as follow:

(1) Use of microbiological methods of food production – the efficiency of micro-organisms, algae, fungi is somewhat greater than that of traditional agricultural animals and plants. This is the rule of biology that works to mean that the smaller the body, the less it is effective (Timoshenko L.V., 1999) [31]. It is easy to trace the following patterns: the time to double the cattle biomass is 30–60 days, 20–40 days for pigs, 2–24 days – for chickens, 6–12 days for grass, 2–6 hours for chlorella, 0.3–2 hours for bacteria and yeast. In other words, the pattern may be depicted as 1440:960:576:288:6:2 in hours.

As it already mentioned, a steady increase in population up to 9 billion people was predicted by 2050 that requires an increase in food sources or forage for the existing agro-ecosystems resulting in even greater impact on the environment. The deficiency in agricultural land, water, forest, fisheries and biological resources is already predicted. High quality edible insects contain protein, vitamins and amino acids wholesome for humans. Insects are known for high food conversion ratio, for example, crickets need six times less than cattle, four times less than sheep, or less than half as compared to pigs and broiler chickens to produce the same amount of protein. In addition, they emit fewer greenhouse gases and ammonia than conventional livestock. Insects can be grown on organic waste.

(2) Artificial reduction in trophic food chains (plant – animal – people), food production directly from autotrophic organisms, namely soy milk, cottage cheese, artificial meat, eggs and so forth (J.D. Mauseth, 2008)[32]. In process of feeding, the potential food energy goes to its consumers. When the potential energy is transferred from unit to unit of the food chain, up to 80–90% is lost as the heat. The longer is the trophic chain, the lower is the production of its last link in relation to that of the initial one.

(3) Mass production of genetically modified foods with specific nutritional and medicinal properties.

One of signs of the next food technology generation is the creation of artificial foods. A. N. Nesmeyanov, the Academician of the USSR, the outstanding chemist laid the basis (1962) of the new research trend, namely the synthetic food creation. He specified the pathway (1960–1970) for the synthesis of simple and available compounds (carbohydrates, nitro compounds, aldehydes), amino acids and natural proteins of products to imitate the smell and taste of food [33]. The caviar product named “Iskra” (abbreviated “black artificial granular caviar”, in Russian “ISKRA”) became the first known industrial design of the protein caviar in the USSR. First in the world, the USSR obtained the caviar at the “Chibis” plant constructed in 1960 at the Institute of Elementorganic Compounds (Moscow). The plant capacity – 1.5–2 kg/h of caviar ready for use. The granular caviar produced at the “Chibis” Plant contains the casein with addition of gelatin, dextrin, starch, glycerin and sodium hydroxide. The taste is added with the fish oil and chemical “flavor of glutominate, etc.” [34, 35].
G. L. Slonimsky, the Doctor of Chemical Sciences who cooperated with A. N. Nesmeyanov in the works of that time stated that: “I flashed with the idea of the caviar molding, so I said I would try to do it. By 1964 we tested our first laboratory samples of the artificial caviar from the skimmed milk. And then, the technology was developed by the Institute by its own resources. Since then, this cheap and delicious product called “Protein Granular Caviar” (based on the casein protein of eggs and other food waste) is manufactured in Moscow and other cities...” [36].

For the first time in the world, the production of the protein caviar was started in the Moscow dock refrigerator. The dairy plant in Myski town in Kuzbass was ranked second in the world in early seventies of the last century (where this industrial technology by Nesmeyanov-Slonimsky was implemented). It was initiated by young leaders of the Kemerovo Institute of Food Science and Technology (KemiIFST founded in 1972) supported by the Kemerovo Regional Committee of the CPSU with members who first tasted the caviar.

The historical tasting procedure at the meeting of the Regional Party Committee Office was attended by Prof. B. Azarov, the Rector of KemiIFST and V. Aret, Ph.D, Vice-Rector of the Research Department. The regional administration authorized to continue the manufacture of this innovative product that required the certain political courage since the production of artificial foodstuff was not acknowledged as the main line of the food programme of the CPSU. Still, sometimes low-expert people spread rumors on production of black caviar from the oil.

Main researches are followed by long-term flow of inventions. For example, ideologically close events are still under development at the institute of the Academician Nesmeyanov.

The range of similar inventions followed first developments at the Nesmeyanov Institute. For example, in 1986, a team of inventors headed by the Academician I. A. Rogov [37] developed the method to manufacture the nutritional protein caviar at the Tbilisi State University. The invention was the use of animal-milk proteins, known as the albumin milk.

Till now, inventors improve various technology aspects using the caviar as the invention by V. A. Gromov in 2003 (V. Gromov, 2003) [38]. The invention will help to create the universal food dye that gives the caviar the color and shade desired.

The next three technology generations can be considered as irrelevant fantasy for evolution. The reason for them lies in reasons other than the increase in human number.

The fourth-generation technology may be called as the nuclear. Signs thereof are as follow:

1. The development of artificial photosynthesis in similar ways of assimilation of nuclear and other energy.
2. Integration of food technology and pharmaceutical products aimed at optimizing and providing individualized human body substances vital for activity.

Fifth-generation technology can be called as the biotechnology that will be followed by genetic, chemical, mechanical and information restructuring of plants, animals and humans. Education and social family functions will be fundamentally restructured.

The sixth-generation technology is quite radical and fantastic. It is as follows: Signs thereof are as follow:

1. Rejection of the protein body as a life carrier, transition to informative electro-magnetic or any other physical field (as per terminology by Vernadsky (2013) [39], that is, the anthroposphere, the final solution to diseases, the beginning and the end of life.
2. Output of life from the Earth planet to the infinite space and its migration to the speed of light, the problem of the fading sun.

CONCLUSION

The history of mankind is the history of “existence of biopolymer bodies capable of self-replication under the constant exchange of matter and energy with the environment” (as defined by the Academician V. Goldansky (1986) [40]. It will be completed and will go to the history of other intelligent system existence capable of self-replication and non-random impact on the environment.

This optimistic path of evolution may be changed in many possible events, including astrophysical and political ways. For example, a huge meteorite will fall on the Earth destroying the entire life. Or, resulting from the military science development and political conflicts a nuclear war will be broken or humans will be contaminated with incurable diseases.

“We face great environmental challenges: climate change, food production, overpopulation, decimation of other species, epidemic disease, and acidification of oceans. In total, they remind that we live the most dangerous live of the humanity evolution. Nowadays, we dispose of the technology to destroy the planet we live on, but we have not developed the ability to escape it, yet. In a few hundred years, we will possibly establish human colonies amid stars, but right now we live on the one planet and we need to work together to protect it. To do that, we need to break, not build up, barriers within and between nations. If we are to stand a chance of doing that, the global leaders need to acknowledge that they failed and keep on failing. When certain people are authorized to use resources at their hands, we will have to learn to share far more than currently we do” (Stephen Hawking, 2016) [41].

Deep analysis of the problem was given in the work Prosekov A. and Ivanova S. [42].

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INTRODUCTION

Currently, in accordance with the adopted State Program for the Development of Healthy Nutrition of the Population of the country, one of the main tasks of scientists in the meat industry and meat producers is to provide products not only for everyday demand but also for preventive purposes. At the same time, it is necessary to take into account the specifics of raw materials supply in the meat industry. In the context of import substitution, it is important to use all available animal protein reserves, for example, horse meat as efficiently and effectively as possible.

The horse meat has a pronounced dietary properties due to a well-balanced amino acid and unique fatty acid compositions. It has hypoallergenic properties and high therapeutic efficiency in the treatment of anemia, hypotrophy and other pathologies.

It is known that horse meat has a high content of mineral substances (calcium, phosphorus, iron – more than 20 kinds in all), essential amino acids, vitamins of group A and B. According to the microelement composition, horse meat is close to beef, but contains more iron and copper involved in the process of hematopoiesis, which is a positive factor in the treatment and prevention of anemia, as well as low sodium and many selenium, which strengthens its dietary properties. Horse meat outperforms other types of raw meat by the content of potassium, vitamins A, E, B1, B2. A horse is an animal with a unicameral stomach, devoid of the gallbladder, possesses meat that is easily digestible. Horse lipids differ significantly from other types of animal fats in chemical composition and biological value. They are fusible (melting point 28–32°C), rich in fatty acids and amino acid compositions. It provides the necessary density and viscosity of the brine, is experimentally justified.

Massaging of salted horse semi-finished products is accompanied by an improvement in their hydrophilic properties, which reach the highest values in 10 hours. The finished experimental product is characterized by better quality and yield (by 6%). Thus, the use of 10% arabinogalactan in a multicomponent brine for horse boiled products makes it possible to improve their functional-technological and taste characteristics.

Keywords: Arabinogalactan, multicomponent brine, horse meat, boiled meat product


vitamin A valuable for human body, contain little cholesterol. However, the finished products from the meat of adult horses are stiff and not succulent, as the muscle fibers of horse meat are larger in comparison with beef fibers of larger diameter and are characterized by a high content of muscle connective tissue [1–5].

To adjust the functional and technological properties (FTP) of boiled products from horse meat, improve their quality and increase yield, the use of multicomponent salting brines is promising [6, 7].

Boiled delicacies, made from whole-muscle pieces of meat, are becoming increasingly popular on the market. To produce such products in order to achieve a gentler consistency, succulence, better slicing – on the one hand, and obtaining additional profit by increasing the yield of finished products – on the other hand, the multi-component brines are used. Due to the peculiarities of its structure and composition delicacy products from horse meat are practically not represented in the consumer market. Multicomponent brines used for the production of whole-muscle meat products are complex disperse systems and the quality and yield of finished products depend on their physico-chemical properties. Their use contributes to the formation of the necessary technological and consumer properties: taste, flavor, softness and color of the finished product. To achieve this effect, and for the purpose of intensifying the brine treatment process, various mixtures containing sugar, spices, sodium nitrite and food acids, phosphates are used. Traditional methods of injecting brines with a high percentage of injection do not allow the finished product to remain marketable, leading to loss of product mass. These disadvantages can be eliminated by increasing the viscosity of stuffing brines due to various additives.

One of the most promising for use in the composition of stuffing brines is arabinogalactan (AG) – highly branched polysaccharide, contained in large quantities in soft wood (TU 9363-021-39094141-08).

The macromolecule of arabinogalactan from larch wood has a highly branched structure; its main chain consists of galactose units linked by glycosidic bonds $\beta$(1→3), and side chains with bonds $\beta$(1→6) from galactose and arabinose units, from single arabinose units, as well as uronic acids, mainly glucuronic acid. The ratio of galactose and arabinose units is approximately 6 : 1. Moreover, AG is mostly extracted from Siberian larch, in which the percentage of this substance is rather high – up to 35%. The resulting compound is an amorphous yellowish white powder, odorless and tasteless. It dissolves easily in water, both hot and cold, does not dissolve in organic solvents and has an average solubility in diluted alcohol. Fig. 1 shows the formula of arabinogalactan.

![Fig. 1. The formula of arabinogalactan.](image-url)

In recent years, studies of the biological activity of AG have intensified dramatically [8, 9, 10]. This is facilitated by such properties as high solubility in water, uniquely low viscosity of brines, narrow molecular weight distribution, and also biodegradability.

Arabinogalactan, a water-soluble polysaccharide, is a source of dietary fiber, is characterized by low toxicity and high biological activity (prebiotic, immuno-stimulating, lipid-lowering, gastro- and hepatoprotective). Especially important are its immunomodulating and prebiotic activity, due to which dozens of biologically active additives to human food and feed additives for animals have already been created in the world. In our country these are Fibrolar, Imbalance, Araglin D, Flarabin, Lakbin and a number of others.

Clinical studies have demonstrated not only the prebiotic and immunomodulatory effects of AG, but also a significant reduction in cholesterol in people with hyperlipidemia [11, 12, 13].

Arabinogalactan is registered under the code E409 in the Code of the Expert Committee on Food Additives of the World Health Organization (FAO/WHO) for food products as a stabilizer of emulsions and thickener. In our country, according to
the List approved by the Chief Sanitary Doctor of the Russian Federation, an adequate level of human AG consumption is 10 g/day, and the upper permissible level is 20 g/day. It is approved for use in the food industry as a thickener, stabilizer and gelling agent [11, 14, 15].

Areas of AG consumption in the food industry are largely determined by its physico-chemical properties: solubility in cold water, low viscosity of concentrated solutions, ability to bind fat and retain moisture, resistance to heating up to 130°C. In connection with the foregoing, it can be concluded that AG is a food additive with high biological value and functional properties acceptable for use in food production [16].

In connection with the foregoing, the aim of the work was to study the possibility of using arabinogalactan polysaccharide in multicomponent brines in the technology of whole-muscle boiled horse meat products to improve the quality of the finished product.

OBJECTS AND METHODS OF STUDY

The experimental part was carried out in the laboratory of the department "Technology of meat and canned products" of the East-Siberian State University of Technology and Management.

For the studies, chilled horse of II fatness category was used. The weight of the horse meat samples was 150 ± 10 g. Brine was stuffed into the control and test samples by means of a syringe. Injections were made along and across the muscle fibers of the meat. The test samples were stuffed with multicomponent brine and massaged in a laboratory unit operating as a tumbler (10 rpm) for 12 hours (in the following mode: the first hour of continuous massaging, the following hours: 40 minutes – massaging, 20 minutes – rest). Sampling was conducted every two hours.

Then the samples were subjected to heat treatment: The product was boiled in water at a temperature of 80–85°C for 30 minutes and heat treated with steam (steam temperature 100°C) for 45 minutes. The finished products were cooled to a temperature of 4–6°C.

The brine quality was determined by physicochemical methods: The kinematic viscosity was determined with the VPZH-2 capillary viscometer, the brine density was measured with a densitometer, and the active acidity was measured by a potentiometric method.

To determine the relationship between the duration of massage, the composition of multicomponent brine, and the properties of salted semi-finished product, the water-retaining capacity (WRC) of the semi-finished product was studied by pressing, the structural and mechanical properties were determined with the Warner-Bratzler instrument and the losses in the heat treatment of the finished product were analyzed by the difference in mass before and after boiling.

The quality of the finished product was evaluated in accordance with the indicators established by regulatory documents for whole-muscle products. Organoleptic indicators were determined on a nine-point scale; mass fractions of sodium chloride — in aqueous extract from the product by the Mor method; sodium nitrite — using photometric method by measuring intensity of the color formed in the interaction of nitrite with sulfonamide and N-(1-naphthyl)-ethylenediamine dihydrochloride in protein-free filtrate; protein — by Lowry's method; lipids — by Soxhlet method; total phosphorus — by photometric method, which is based on the reaction of phosphorus with ammonium molybdate in the presence of hydroquinone and sodium sulfite to form a colored compound, the color intensity of which is measured photometrically; residual activity of acid phosphatase - photometrically depending on the intensity of the resulting color, expressed by the mass fraction of phenol, the content of arabinogalactan - by gel permeation chromatography in a glass column with dextran calibration.

For conducting experimental studies, the standard salting brine used in the technology of whole-muscle meat products was taken as the starting material [17]. According to the Technical Regulations of the CU 034/2013, meat producers should use salt-nitrite mixtures instead of sodium nitrite in their production, so, in addition to sodium chloride, a salt-and-nitrite mixture Solino 0.5/0.6 was added. Thus, the standard brine included: Sodium salt, saline-nitrite mixture 0.5/0.6 and sucrose. As a control, a standard brine was used with the addition of phosphates and sodium erythorbate. For further studies, the dose of control brine and the amount of salting ingredients according to the FTP were chosen: water-retaining capacity and losses during the heat treatment of the boiled product. Brines were introduced by stuffing in an amount of 20 to 80% of the raw material weight. Samples with 40% brine injection had larger WRC and a smaller amount of losses during heat treatment. The content of salting ingredients (kg) per 100 liters of control brine (with injection in an amount 40 %): Table salt – 4 kg, salting-nitrite mixture – 1.5 kg, sucrose – 1.4 kg, phosphate – 0.5 kg, sodium erythorbate – 0.5 kg.

Currently, in the meat processing industry in the production of whole muscle products carrageenans are used as food hydrocolloids. Different types of carrageenans were added to the experimental samples of brines: kappa carrageenan Bengel 270 and iota-carrageenan MB-150F in an amount of from 0.2 to 1.5% of the brine weight. The control was a basic brine (Table 1).
### RESULTS AND DISCUSSION

At the first stage, the properties of brines were studied. The data given in Table 1 indicate that carrageenans increase density and viscosity of brines, but behave differently. Iota-carrageenan, in contrast to kappa-carrageenan, expands in a cold brine and the brine viscosity increases with its increase from 0.2 to 1.5% by a factor of 1.5–12 as compared to brines containing the same amount of kappa- carrageenan, respectively. Increased viscosity of the brine with iota-carrageenan to a certain extent allows to reduce its losses between injection and massaging. On the other hand, a high viscosity of the brine can lead to clogging of the injector needles.

Kappa-carrageenans expand when heated, providing a high WRC in the finished product. The obtained data show that the dose of carrageenans providing satisfactory parameters for density, viscosity and pH of brines for kappa-carrageenans does not exceed 1%, and iota-carrageenans – 0.5%. In the studied brines, the total content of iota-and kappa-carrageenans was taken in an amount of 1% of the brine weight, with recommended doses of inection into meat products from 0.5 to 2%. Analyzing the experimental data on the kinematic viscosity of brines from the technological point of view, the most acceptable is injection of 0.2% of iota-carrageenan; since the total content of carrageenans is taken in the amount of 1%, the kappa-carrageenan content is 0.8%, thus, the kappa-iota-carrageenan ratio is 4 : 1.

The important structure-forming components used in the technology of production of whole-muscle meat products are protein preparations. Soy and animal proteins are most often used for this purpose.

In connection with the foregoing, soy isolate Supro 595 and animal protein Promiat-90, in concentrations not exceeding the maximum levels of their use in the technology of production of meat products, were injected into brines with carrageenans. The analysis of the data showed that all brines are acceptable in their physicochemical parameters. However, a sample injected with brine, which included a soy isolate, received a relatively low organoleptic evaluation because of the characteristic taste of soy.

Currently, producers of meat products are increasingly using brines with proteins of animal origin, as the demand for products containing soybeans has fallen markedly. On the basis of the physicochemical indices of the experimental brines and the organoleptic evaluation of the final product, the optimal brine formulation was chosen, including the animal protein and carrageenans (Table 2).

One of the main properties of thickeners of different origin (polysaccharides, proteins) is mutual synergism, when the functional activity of the mixture exceeds the sum of the activities of the components. Against the background of carrageenan, protein preparations significantly reduce product losses during heat treatment, and finished products are less susceptible to the process of syneresis.

At the next stage of the study, the influence of the dose of arabinogalactan on the parameters characterizing the brine quality was studied. Such parameters include kinematic viscosity, density and active acidity of brines. In the experimental brines, AG was added in the amount from 5 to 15% (with increment of 5%). The control was the optimum brine formulation shown in Table 2. The experimental data are presented in Table 3.

### Table 1. Characteristics of brines with carrageenans

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Control</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Kappa-carrageenan</strong></td>
</tr>
<tr>
<td></td>
<td>Density, kg/m³</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>1056.0</td>
<td>1056.0</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>6.3</td>
</tr>
<tr>
<td>Kinematic viscosity, mm²/sec</td>
<td>1.3892</td>
<td>1.4412</td>
</tr>
</tbody>
</table>

### Table 2. Brine formulations

<table>
<thead>
<tr>
<th>Ingredients, kg per 100 kg of brine</th>
<th>Control</th>
<th>Optimum brine composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table salt</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>Nitrite curing mixture Solino 0.5/0.6</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>Sucrose</td>
<td>1.40</td>
<td>1.40</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Sodium erythorbate</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Animal protein</td>
<td>–</td>
<td>0.75</td>
</tr>
<tr>
<td>Kappa-carrageenan Bengel 270</td>
<td>–</td>
<td>0.80</td>
</tr>
<tr>
<td>Iota-carrageenan MB-150F</td>
<td>–</td>
<td>0.20</td>
</tr>
<tr>
<td>Water</td>
<td>92.10</td>
<td>90.35</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Table 3. Characteristics of multicomponent brines

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Control</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, kg/m³</td>
<td>1056.00</td>
<td>1082.00</td>
<td>1094.00</td>
<td>1123.00</td>
</tr>
<tr>
<td>Kinematic viscosity, mm²/s</td>
<td>1.4892</td>
<td>1.9876</td>
<td>2.4932</td>
<td>2.8893</td>
</tr>
<tr>
<td>pH</td>
<td>7.04</td>
<td>6.04</td>
<td>5.68</td>
<td>5.28</td>
</tr>
</tbody>
</table>

In the study of brines, it was found that when the amount of injected AG is increased, the density of experimental brines increases insignificantly compared to the control brine. The kinematic viscosity increases with increasing content of AG in the brine, however, is at a level allowing injecting brines by means of stuffing, achieving its rapid distribution in the product.

The active acidity of the brine with increasing the AG injection dose is reduced. This is due to the fact that the active acidity of the pure AG solution is in the range of 4.0 to 4.5. It is known that the area of the most effective action of most of the brine ingredients (pH = 6–7). In this regard, to increase the active acidity of the brine and binding of calcium ions, it was decided to increase the dose of phosphate within the acceptable value to 1.2% [18]. This will increase the moisture-binding ability and softness of meat, stabilize the color, inhibit the oxidation of lipids. These changes in the active acidity of brines with AG at a phosphate content of 1.2% of the brine weight are presented in Table 4.

Table 4 shows that the experiment with 10% arabinogalactan and the phosphate content of 1.2% is the most satisfying to these requirements. Thus, for further study, experimental brine 2 with a 10% AG content was selected.

The compositions of the control and experimental brines are presented in Table 5.

When 40% brine containing 10% AG is added to the unsalted meat, the content of AG in the finished product is about 3 g per 100 g of product, taking into account the loss of loosely bound moisture. Physiologically useful effects were established in humans with consumption of 1.5 to 4.5 grams of AG per day [13]. In accordance with the recommendations of the Expert Committee on Food Additives of the World Health Organization (WHO), a product which contains 3 g of dietary fiber per 100 g is considered a source of dietary fiber.

At the second stage, the relationship between the duration of horse meat massaging in the salting process and the quality indices of the salted semi-finished product was studied.

To study the effect of the composition of a multicomponent brine with 10% AG content and the period of massaging, in the salt semi-finished product, the mass fraction of moisture, the moisture-binding capacity (MBS) and WRC-indicators were measured, which are related to the quality and yield of meat products.

Table 4. Brine active acidity

<table>
<thead>
<tr>
<th>Samples</th>
<th>Amount of arabinogalactan injected, %</th>
<th>pH of brines with a phosphate content of 1.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>8.28</td>
</tr>
<tr>
<td>Experiment 5</td>
<td>5</td>
<td>7.68</td>
</tr>
<tr>
<td>Experiment 10</td>
<td>10</td>
<td>6.82</td>
</tr>
<tr>
<td>Experiment 15</td>
<td>15</td>
<td>5.94</td>
</tr>
</tbody>
</table>

Table 5. Brine compositions

<table>
<thead>
<tr>
<th>Ingredients, kg per 100 kg of brine</th>
<th>Control</th>
<th>Brines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>Nitrite curing mixture Solino 0.5/0.6</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>Sugar</td>
<td>1.40</td>
<td>1.40</td>
</tr>
<tr>
<td>Phosphate</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>Sodium erythorbate</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Animal protein Promiat - 90</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Kappa-carrageenan MB-150</td>
<td>–</td>
<td>0.80</td>
</tr>
<tr>
<td>Iota-carrageenan Bengel 270</td>
<td>–</td>
<td>0.2</td>
</tr>
<tr>
<td>Arabinogalactan</td>
<td>–</td>
<td>5.00</td>
</tr>
<tr>
<td>Water</td>
<td>90.65</td>
<td>84.65</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
The analysis of the obtained data showed that the mass fraction of moisture in the salted semi-finished product increases with the duration of massaging from 2 to 12 hours and 10 hours higher than in the initial measurement by 7–14% both in the control and in the test samples. The results of experimental studies of MBC of a salted semi-finished product are presented in Fig. 2.

The results of experimental studies of the water retention capacity of salted horse meat after heat treatment are shown in Fig. 3.

The data in the figures are presented in relative units, in order to exclude the influence of the raw material properties.

The analysis of the obtained data showed that with increasing duration of massaging MBC and WRC of the control and test samples increase and reach the maximum values during massaging for 10 hours, while the difference between the control and the test samples is 5.8% and 6.3%, respectively. The values of MBC and WRC in the control and test samples correlate in the process of massaging the samples. But in test samples with AG these values are higher in comparison with the control due to the complex carbohydrates contained in arabinogalactan and their branched structure. Reduction of MBC and WRC at a longer massaging can be explained by partial denaturation of proteins.

**Fig. 2.** Dynamics of change in moisture-binding capacity of salted semi-finished product from horse meat.

**Fig. 3.** Dynamics of change in the water-retaining capacity of the finished product.
Based on the FTP of the salted semi-finished product, the duration of mechanical treatment for 10 hours was selected. The next stage of the study was evaluation of the quality and yield of the finished product. In connection with the task, the quality of the samples was evaluated in accordance with regulatory documents for whole-muscle products. In addition, the FTP and the structural and mechanical properties (SMP) of the control and test samples subjected to massaging for 10 hours were studied (Fig. 4).

An analysis of the results indicates that the best characteristics have the prototype, which has the great plasticity and the less cutting force. The lower the cutting force, the softer the product. The sample has a high WRC and, accordingly, the highest yield after heat treatment – 92%.

The results of study on models allow us to establish the patterns of changes in properties and yield of products when changing recipes, technologies and regimes. The product was boiled in water at a temperature of 80–85°C for 30 minutes and heat treated with steam (steam temperature 100°C) for 45 minutes. The criterion for evaluating the method was the loss during heat treatment. In the course of the conducted studies, it was found out that the losses in cooking with a live steam are lower by 5% than when boiling in water.

The quantitative values of the losses of the finished product during the heat treatment are shown in Table 6.

In the course of the experiment, it was found that after 10 hours of massaging, the losses are reduced in the control sample by 54%, and in the experimental sample by 73%, i.e. the difference between the samples is 19%.

An organoleptic evaluation of the horse meat product with a brine containing 10% AG (“Delicacy horse meat”) was carried out on a 9-point scale (Fig. 5).

From the profile record it can be seen that the organoleptic evaluation of the product “Delicacy horse meat” is higher in all indicators, in comparison with the control. Particularly noticeable is the difference in assessment of the consistency, succulency and appearance of the products. In the control sample, the consistency and succulency was evaluated by 6 points, as it was rigid and dry, which correlates with the MBC and the cutting force.

Qualitative parameters of the boiled product “Delicacy horse meat” are presented in Table 7.

![Fig. 4. Structural and mechanical properties of control and test samples.](image)

### Table 6. Losses at boiling of salted semi-finished product

<table>
<thead>
<tr>
<th>Heat treatment losses, %</th>
<th>Duration of massage, hour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Control</td>
<td>31.9 ± 0.3</td>
</tr>
<tr>
<td>Experiment</td>
<td>31.2 ± 0.5</td>
</tr>
</tbody>
</table>
Table 7. Qualitative parameters of the boiled product “Delicacy horse meat”

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Quality requirements as per GOST 32785-2014. Products of horse meat</th>
<th>Horse meat delicacy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>The surface is clean, dry with no meat scraps, no fringes, spices and bay leaves</td>
<td>The surface is clean, dry with no meat scraps, no fringes, spices and bay leaves</td>
</tr>
<tr>
<td>Shape</td>
<td>Rectangular, oval, cylindrical</td>
<td>Rectangular, oval, cylindrical</td>
</tr>
<tr>
<td>Consistence</td>
<td>Elastic</td>
<td>Elastic</td>
</tr>
<tr>
<td>Cut color</td>
<td>Uniformly colored muscular tissue from light red to dark red</td>
<td>Uniformly colored muscular tissue from light red to dark red</td>
</tr>
<tr>
<td>Taste and flavor</td>
<td>A pleasant taste and flavor</td>
<td>A pleasant taste and flavor</td>
</tr>
<tr>
<td>Weight ratio of table salt, %</td>
<td>max. 3.0</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>Weight ratio of sodium nitrite, %</td>
<td>max. 0.005</td>
<td>0.0030 ± 0.0001</td>
</tr>
<tr>
<td>Weight ratio of protein, %</td>
<td>min. 14</td>
<td>16.5 ± 0.3</td>
</tr>
<tr>
<td>Weight ratio of fat, %</td>
<td>max. 12</td>
<td>4.00 ± 0.06</td>
</tr>
<tr>
<td>Weight ratio of total phosphorus in terms of P₂O₅, %</td>
<td>max. 0.8</td>
<td>0.300 ± 0.003</td>
</tr>
<tr>
<td>Residual activity of acid phosphatase, %</td>
<td>max. 0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Content of arabinogalactan, g/100 g of product</td>
<td>–</td>
<td>3.0</td>
</tr>
</tbody>
</table>

These parameters indicate the compliance of the boiled product “Delicacy horse meat” with the requirements of regulatory documents for whole-muscle meat products.

**CONCLUSIONS**

The use of arabinogalactan in brines provides their density and viscosity; the pH level of such a brine is close to the pH level of the most effective action of the brine ingredients. Massaging the salted semi-finished horse meat is accompanied by an improvement in the functional-technological and structural-mechanical properties of horse meat, which reach their maximum values after 10 hours. The finished experimental product is characterized by better quality and yield (by 6%).

It has been established that the use of arabinogalactan in multicomponent brines for cooked horse meat products allows to improve the taste characteristics of the finished product.

EFFECTS OF PROPIONIC-ACID BACTERIA AND BIFIDOBACTERIA ON THE QUALITY OF RAW SMOKED SAUSAGES

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Abstract: Propionic-acid bacteria and bifidobacteria are widely used in food industry. Therefore, it is important to determine their biochemical activity and their aroma producing potential. In this study, the effect of the use of propionibacteria and bifidobacteria as starter cultures on the sensory characteristics of raw smoked sausages has been studied. The sausages were prepared with starter culture consisted of Propionibacterium shermanii KM-186 and Bifidobacterium longum B379M and compared with the sausages with a commercial starter culture Bitec LS-25. The results have shown, that the sausages containing starter culture of propionic-acid and bifidobacteria, obtained better sensory scores, better quality characteristics compared to the sausages made with commercial starter culture. The analysis of volatile compounds has shown, that the addition of starter culture, containing propionic-acid bacteria and bifidobacteria leads to formation of additional compounds, including lactones, phenols, and terpenes. During sensory evaluation, experts noticed the presence of mild creamy note in experimental sample. It can be the result of lactones formation by propionic-acid bacteria and bifidobacteria. In addition, it was shown that the addition of propionic-acid bacteria and bifidobacteria reduces nitrite amount in sausages in several times (11 times approximately compared to commercial starter culture) due to nitroreductase activity of these bacterial strains.

Keywords: Raw smoked sausages, propionic-acid bacteria, bifidobacteria, starter cultures, volatile compounds, flavor, sausages

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INTRODUCTION

The characteristic taste and aroma of fermented sausages originates from the breakdown of carbohydrates, lipids, and proteins through the action of microbial and endogenous meat enzymes [1]. The aroma is a combination of many different non-volatile and volatile compounds. Some originate from added spices, others are metabolic or chemical products derived from carbohydrates, lipids and proteins during the fermentation and drying periods. Microbial growth in the sausage mince, together with the activity of enzymes from the meat and fat, are undoubtedly responsible for many of those components. However, antioxidative reactions initiated by metallo-compounds or other factors may be of great importance as well [2, 3].

Many volatile compounds have been identified in fermented products [4]. The volatile compounds produced during maturation of dry meat products may be of non-enzymatic origin, as during self-oxidation of lipids, or may result from a catalysis. This catalysis is due to endogenous enzymes in the case of non-inoculated products such as dry-cured ham, but depends also on exogenous enzymes in the case of fermented meat products [2].

It is unknown, which processes play the major role in the desirable aroma development of fermented sausages. One of the most studied of processes is the breakdown of triglycerides into free fatty acids, di- and monoglycerides during ripening and the increase of different carbonyl oxidation products like aldehydes and ketones [1].

Lipid oxidation is a reason of formation of the generation of nonbranched aliphatic compounds such as alkanes, alkenes, methyl ketones, aldehydes, alcohols and several furanic cycles. Compounds of low molecular weight form during the fermentation, for example, diacetyl, acetoin, butanediol, acetaldehyde, ethanol, acetic acid etc. [1].

Carbonyl compounds probably have an impact on flavor as they generally have very low sensory threshold values in the ppm to ppb range. Since fatty acids are precursors of carboxyls, lipolytic activity of the microorganisms present in the mince is believed to be of great importance and has been much investigated. However, it is doubtful whether large amounts of free fatty acids are necessary in obtaining the amount of oxidation products demanded for the characteristic sausage flavor, especially when carboxyls may arise from the intact triglycerides as well as from the free fatty acids.

Starter cultures are used in the meat industry to start and propagate the fermentation process, extend the shelf life of the product, improve its hygienic quality

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and increase the acceptability of the final product [5]. There are many technologies of meat products, made with the use of starter cultures [6, 7, 8, 9].

Propionic-acid bacteria (PAB), the most abundant flora during ripening of Swiss-type cheeses, are directly involved in the characteristic eye formation and in the production of propionic and acetic acids. Also they play a key role in the formation of cheese flavor [10, 11, 12]. However, they are not widely used in meat industry.

Propionic-acid bacteria grow at low oxygen concentrations (anaerobic to aerotolerant) [13] and their growth is inhibited by high salt-in-moisture (S/M) levels, to an extent dependant on strain type [14, 15, 16]. PAB grow optimally between pH 6 and 7 with a pH maximum for growth at 8.5 and minimum at 4.6 [15, 17]. Cheese pH controls the rate of growth and metabolism of PAB [18] and a higher inocula is required for cheeses with a lower cheese pH [13]. The optimal growth temperature for PAB is 30°C, but growth also occurs between 7 and 45°C as reviewed by Langsrud et al. [15]. Park et al. [7] reported that 16 out of 33 strains of PAB tested grew at 7.2°C and 31 out of 33 grew at 12.8°C. No growth of P. freudenreichii was reported at 2.8°C.

Also dairy PAB have only a few nutritional requirements. Many PAB strains grow in the absence of organic nitrogen sources, in a basal medium containing a carbon and energy source, ammonium, minerals, and 2–4 vitamins (at least pantothenate and biotin are required) [11, 19, 20].

One of the important properties of PAB for use in meat industry is their proteolytic activity. A proteolytic system was found in all the species of dairy Propionibacterium [21]. Searles et al. [22] reported that propionic-acid bacteria, in a medium with acid casein, were able to increase the trichloroacetic-acid (TCA)-soluble nitrogen. Later, El Soda et al. [23] found a "general caseinolytic activity" in three strains of Propionibacterium freudenreichii and in one strain of P. acidipropionici. Intracellular peptidases have been studied in more details [15, 24, 25] found peptidases able to release proline into the medium. Perez Chaia et al. [26] showed that leucine aminopeptidase and proline aminopeptidase have the good activities in P. freudenreichii. This proline aminopeptidase was purified and characterized [27]. El Soda et al. [23] also found prolyl dipeptidyl aminopeptidase activity [21].

Propionic-acid bacteria produce some volatile compounds, which are important for cheese flavor. Thierry et al. [19, 20, 28, 29] studied the formation of these compounds by PAB in cheese. Compounds produced by PAB, which are responsible for flavor of cheese, are acetic, propionic and butanoic acids and 2-methyl and 3-methylbutanal. P. freudenreichii for example, produces flavor compounds of varied origins (fermentation, lipolysis, amino acid catabolism). The work of Thierry et al. [28] showed, that various biochemical changes were observed in Raclette cheeses with the addition of Propionibacterium freudenreichii compared to the control cheese: the fermentation of lactate to propionate and acetate, a marked enhancement of lipolysis, some modifications of the amino acid profile, the conversion of branched chain amino acid to a variety of aroma compounds, and the increase in other volatile compounds such as esters and ketones.

Bifidobacteria are mainly added to food products, because of their probiotic properties [30, 31, 32, 33]. Bifidobacteria, naturally present in the dominant colonic microbiota, represent up to 25% of the cultivable faecal bacteria in adults and 80% in infants. As probiotic agents, bifidobacteria have been studied for their efficacy in the prevention and treatment of a broad spectrum of animal and/or human gastrointestinal disorders, such as colonic transit disorders, intestinal infections, and colonic adenomas and cancer [32]. Mainly bifidobacteria are used in dairy industry as a component of fermented drinks, but also they are used as a starter culture (in combination with other bacteria) during the production of fermented sausages [31].

According to [34] the use of combined concentrate of propionic-acid bacteria and bifidobacteria has positive effect on sensory profile of dry smoked sausages. New compounds are formed as a result of bacterial action. The content of free fatty acids in the sample with these bacteria is by 20–30% higher than in traditionally produces sausages. It can be result of higher lipase activity of propionic acid bacteria and bifidobacteria. The main difference between the samples was in high amount of lactones in the experimental sample. A weak pleasant creamy tone in the aroma and flavor of the experimental sausage, obtained using propionic acid bacteria and bifidobacteria, probably, the result of presence of lactones in experimental sample.

Considering the above, the effect of propionic-acid bacteria on flavor development of fermented sausages is interesting issue to study. Thus, this work was conducted to investigate the potential benefit from the use of Propionibacteria and Bifidobacteria as starter cultures during the production of raw smoked sausages and their influence on the quality characteristics and chemical composition of sausages. The investigation of the influence of starter culture addition and flavor compounds as well as sensory evaluation, are very interesting objects to study. To determine this effect, sausages with starter culture of propionic-acid and bifidobacteria were compared with sausages with commercial starter culture.

**OBJECTS AND METHODS OF STUDY**

**Manufacture and sampling.** The sausages, used in this study, have been produced at the local factory (Republic of Buryatia, Russia). Ingredients of sausages are listed in Table 1. Mean values of results of three experiments were taken.

Raw smoked sausages were produced by using beef, lean pork, pork fat, NaCl, NaNO₂, sugar, brandy and spices. On the first step meat was minced, mixed with salt, spices and brandy. On the second step the 5 %-solution of sodium nitrite, brandy, lean pork, pork fat and spices were added. After mincing of meat and mixing, the mixture was divided into two batches: batch A was inoculated with 1cm³ of starter culture.
containing propionic-acid bacteria and bifidobacteria (LLC Small Commercial Enterprise “Bifivit”, Ulan-Ude, Russia) per 100 kg of raw meat, while the commercial starter culture Bitec LS-25 (Frutarom, Germany) was added to batch B was added with a concentration of 0.025%.

Table 1. Composition of raw smoked sausages with starter culture

<table>
<thead>
<tr>
<th>Materials and ingredients</th>
<th>Percentage share</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Basic ingredients</strong></td>
<td></td>
</tr>
<tr>
<td>Beef</td>
<td>35%</td>
</tr>
<tr>
<td>Lean pork</td>
<td>35%</td>
</tr>
<tr>
<td>Pork fat</td>
<td>30%</td>
</tr>
<tr>
<td><strong>Additional ingredients and spices (in kg to 100 kg of basic ingredients)</strong></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>3.5 kg</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>0.01 kg (in 5%-solution)</td>
</tr>
<tr>
<td>Sugar</td>
<td>0.2 kg</td>
</tr>
<tr>
<td>Brandy</td>
<td>0.25 kg</td>
</tr>
<tr>
<td>Starter culture</td>
<td>1 cm²</td>
</tr>
<tr>
<td>Black pepper</td>
<td>0.15 kg</td>
</tr>
<tr>
<td>Allspice</td>
<td>0.05 kg</td>
</tr>
<tr>
<td>Cardamom or Nutmeg</td>
<td>0.05 kg</td>
</tr>
</tbody>
</table>

Experimental starter culture contained strains Propionibacterium shermanii KM-186 and Bifidobacterium longum B379M. Cell counts of each strain were 10 log CFU/cm². The starter culture was in the liquid form.

Commercial starter culture Bitec LS-25 contains strains Staphylococcus carnosus and Lactobacillus sakei. Total cell counts is 1.5 * 10 log CFU/g. The consistency of the starter culture was fine-grained, freeze-dried powder. The producer claims, that the starter culture creates a rapid acidification process and a typical fermentation aroma, accelerates color formation, improves color stability, fat stability and consistency. The strain of lactobacillus contained is highly suited to compete with the spontaneous flora.

The meat mixture was immediately stuffed in natural casings to obtain sausages with an initial weight of approx. 1400-1500 g, a length of approx. 60 cm.

The process of thermal treatment was carried out in the same termoagregate with automatic control for (3–4) days. On the first day sausages were kept at temperature 24°C, relative humidity 92.3% and air velocity (0.2–0.5) m/s. The temperature was then lowered to (22–20)°C and kept for one day. On the third day sausages were smoked for 4–6 hours, the relative humidity was reduced to 88.3%. Then, on the fourth day smoke intensity was increased, and process was carried out at (20 ± 2)°C, relative humidity (83.3%) and air velocity (0.05–0.1) m/s. The total duration of treatment was a total of 8–12 hours.

The process of drying was carried out in the same termoagregate at (18 ± 2)°C and relative humidity 82.3% for 1 day. Further drying was carried out at temperature (13 ± 1)°C, relative humidity (77.3%) and air velocity (0.05–0.10) m/s for (17–20) days.

**Microbiological analysis.** Sausage samples (10 g) were homogenized with 90 ml distilled water. Decimal dilutions were prepared. Microbiological analyses were performed every day during 10 days of ripening.

The numbers of propionic acid bacteria were determined on GMK-1 medium (Biocompas-S, Russia), consisting of corn-milk mixture (30 g), peptone (30 g), lactose (18 g), ascorbic acid (1 g), sodium citrate (12 g), magnesium sulphate (0.24 g), potassium phosphate (monobasic) (4 g), sodium phosphate (dibasic) (2 g), agar (6 g), distilled water (2000 ml). Incubation was performed at 30°C for 5 days.

Bifidobacteria counts were determined using Blaurock medium (Blaurock, 1937) with neomycin (0.2 ml of solution of neomycin was added to 20 ml of medium). For getting of neomycin solution one bottle of neomycin (500000 ME) was dissolved in 50 ml of distilled water. Colonies were counted after incubation at 37°C after 3 days.

**Chemical analysis.** Analyses of the moisture content, pH, and NaNO₂ contents were performed in triplicate. The moisture content of dry-fermented sausages was determined by dehydration at 103°C to constant weight by the ISO recommended methods (ISO, 1997). The pH was measured using a pH-150M pH meter (Gomel plant of measuring devices, Belarus).

Nitrite amounts were analyzed using spectrophotometric method on KFK-3 (Zagorsk optical and mechanical plant, Russia).

**Sensory evaluation.** The sensory evaluation was performed by nine trained experts. The experts were asked to evaluate sensory characteristics of the sausages. The sausage samples were sliced (the thickness was approximately 2 mm). Control and experimental batches were numbered and provided to each expert with degustation card. The sensory evaluation was conducted in individual rooms. Six sensory characteristics were evaluated by judges. General appearance, color, aroma, texture, taste, and juiciness were the attributes, evaluated during sensory analysis. The hedonic scale from 1 (extremely poor/unacceptable) to 9 (extremely acceptable) was used in the study. The mean values of all experts’ marks for each characteristic were calculated.

**Gas chromatography.** To extract volatile substances sausage samples (100 g) were minced, placed into 2-l flask. Content of volatile compounds was determined by gas chromatography (GC) using gas chromatograph Hewlett-Packard 5730 (Hewlett-Packard, USA) equipped with a flame ionization detector and capillary column SPB-1 (50 m * 0.32 mm, 0.25 µm) (Supelco, USA). Chromatographic conditions were as follows: isotherm at 60°C for 5 minutes, then the temperature programming to 250°C. Helium gas velocity through the column was 1.5 ml/ min. The identification of peaks in the sample chromatograms was performed using a system for the processing of chromatographic data Ecokhrom (Russia). The concentration of individual components expressed as µg/100 g of product.

**Statistical analysis.** The data obtained for pH, moisture content, nitrite amounts, volatile compounds,
sensory characteristics was assessed statistically to determine significant differences between products for these parameters. Analyses of each parameter were carried out in triplicate at various sampling times. Mean, standard deviation and standard error were calculated for all quantified variables. An analysis of variance (ANOVA) was carried out. Significance level P < 0.05 was used for all data. All the statistical analyses were performed using programs Statistica 6.0 and Microsoft Excel 2010.

RESULTS AND DISCUSSION

Microbiological analysis

The results for analysis of counts of propionic-acid bacteria and bifidobacteria are shown in Fig. 1. In both samples, we can see increasing amount of bacteria during the production process.

![Graph showing changes in growth of propionic-acid and bifidobacteria in raw-smoked sausages](image)

Fig. 1. Changes in growth of propionic-acid and bifidobacteria in raw-smoked sausages.

The initial quantity of probiotic microorganisms was approximately 5 log CFU/g. The quantity of viable cells of bifidobacteria and propionic-acid bacteria has gradually increased starting from second day of manufacturing. After 3 and 4 days the quantities of bifidobacteria were 9 log CFU/g and 10 log CFU/g, the quantities of propionic-acid bacteria were 10–11 log CFU/g. Sausages contained approximately 11–12 log CFU/g bifidobacteria and the same amount propionic-acid after 5 days of manufacturing. This amount of bacteria was stable during the smoking and drying.

The results of research have shown that PAB are resistant to high concentrations of NaCl and low temperatures during salting. The results of the study have shown that propionic acid bacteria and bifidobacteria can survive and grow in meat due to low nutrition requirements of bacteria and their ability to survive at low positive temperatures. This fact makes possible to use these bacteria for production of fermented sausages.

Results of chemical analysis

Results for analysis of pH are shown in Fig. 2. The initial pH of control sample was 6, the pH of sample with starter culture was 5.95, pH values of both samples drastically decreased after 5 days of fermentation. The decrease in sample with experimental starter culture was bigger, than in control sample. The pH values in both samples have slowly increased after (had increased) 10 days of fermentation due to proteolysis of proteins and formation of products of their decomposition. The pH value is close to isoelectric point after 20 days of fermentation.

The moisture content is one of the main characteristics of meat. For raw sausages it is very important. The development of structure of product and overall microflora also depend on the moisture content. In further studies the impact of combined concentrates to moisture content changes in the raw sausage during its production was studied.

The Fig. 3 shows, that water content after 5–10 days in experimental sample is lower, than in control sample. It is related to intensive decreasing of pH value during this period. The loss of water in experimental sample in 15–20 days of manufacture was 24–34%, on the other hand, the loss in control sample 20–30%. The difference in water loss was approximately 4%. After 20 days of manufacture the moisture content in control samples was 27.3%, the same value in control samples was just after 25 days of manufacture.

![Graph showing changes in moisture content](image)

Fig. 2. The changes in pH of raw-smoked sausages added with propionic-acid bacteria and bifidobacteria.

![Graph showing effect of addition of starter cultures](image)

Fig. 3. Effect of the addition of starter cultures of propionic acid bacteria and bifidobacteria on the changes in moisture content.
The main chemical characteristics of control and experimental samples are shown in Table 2. The results show that moisture, protein and ash content were approximately the same in both samples. The difference in NaNO₂ content was found between samples. NaNO₂ content in experimental sample was 0.00036, and in control sample was 0.0040.

One of the main factors, which form quality of raw-smoked sausages, is pH. When pH values are close to 5.2–5.3, there is swelling of collagen hydrolysis-linking and activation of cellular enzymes, especially cathepsins. At the same value the development of pathogenic and toxicogenic bacteria suppresses. In this regard, the pH value was the main criterion for establishing the dose contributed bacterial concentrates in sausages. Therefore, the different amounts of bacterial concentrate were inoculated in the model samples of minced raw sausages.

It is well known that meat with pH value, which is close to isoelectric point, has the lowest water holding capacity. The lower water holding capacity can accelerate the drying process. In experimental sample pH values were closer to the isoelectric point than in control sample, probably, it is the reason of lower moisture content in this sausage. pH values close to isoelectric point can be a reason of better consistency of the product. The results of the study have shown that the bacterial concentrate of propionic acid and bifidobacteria can reduce the time of manufacturing process that can have good practical application.

Nitrite has a number of functions in the curing of meat: it is involved in the development of color and odor; it has a preserving and antioxidant effect. Nitrite added in the formulation is reduced to nitric oxide, which interacts with meat pigments (myoglobin) to form nitrosomyoglobin and gives the characteristic cured red meat color. Some authors reported that addition of some propionic-acid bacteria strains can reduce nitrite content in products. According to [35] propionic-acid bacteria have different probiotic properties including reducing nitrates and nitrites with formation of nitrogen monoxide. Nitrate reduction is currently considered to be a key characteristic for the determinative grouping of strains of the Propionibacterium. In work [36] it was proven that strains of *P. acidipropionici*, *P. acnes* and *P. freudenreichii* subsp. *freudenreichii* are able to reduce nitrate on the yeast extract lactate and yeast extract media. It was found that nitrate reduction was strongly influenced by environmental factors such as oxygen, nitrate concentration, pH, media composition, incubation period and the presence of glucose [36]. As it was reported some strains of genes Propionibacterium can reduce nitrate to nitrile and further to nitrous oxide (N₂O) due to action of enzymes such as nitrate reductase.

Bifidobacteria can also eliminate nitrite by non-enzymic mechanism with generation of nitric oxide [37, 38]. The results of the present research correspond to results of previous research works. The content of NaNO₂ in experimental sample (0.00036%) was lower than in control sample (0.0040%) in several times (11 times approximately). It means more complete breakdown of NaNO₂ and its transformation to nitrosopigments by bacteria included in starter culture.

We can conclude that the use of combined bacterial concentrate of propionic-acid and bifidobacteria as a starter culture reduces nitrite content and processing time of meat products.

**Sensory evaluation**

Sensory analysis is one of the most valuable factors in quality evaluation and assessment. It is especially important for evaluation of new products. The sensory profiles of raw smoked sausages are shown in Fig. 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>Control</td>
<td>27.0 ± 1.2</td>
</tr>
<tr>
<td><em>P.shermanii + B.longum</em></td>
<td>26.5 ± 1.3</td>
</tr>
</tbody>
</table>

Fig. 4. Sensory profile of raw-smoked sausages.
There were better scores in experimental sample compared to control. Experimental samples had more intensive and pleasant aroma, and mild flavor with a sour milk tone. Consistency of experimental samples was more homogeneous compared to the control. The color characteristics were also different. Sample with propionic-acid and bifidobacteria was dark-red, and it had more uniform color.

The results of sensory analysis have shown that the sample with propionic-acid and bifidobacteria got higher scores in all sensory characteristics. It can be a result of action of starter culture on texture and flavor of products. Thus, the results show positive impact of combined concentrates to organoleptic properties of raw sausages.

Identification of volatile compounds

In the study approximately 140 substances were detected using gas chromatography (GC) and 85 of them were identified. The results from the GC analysis are shown in Table 3. It was found that the main volatile compounds of the sausages are saturated and unsaturated aliphatic aldehydes, alcohols, ketones, lactones, and fatty acids.

All identified compounds were grouped in nine classes including aldehydes, ketones, phenols, esters, terpenes, carbohydrates, alcohols, carboxylic acids, lactones. The content of volatile compounds in raw-cured sausages in percent is shown in Table 4. The most dominant classes of volatiles were Carboxylic acids, Phenols and Aldehydes.

### Table 3. Beginning. Volatile compounds in fermented sausages

<table>
<thead>
<tr>
<th>№ of peak</th>
<th>Retention Index</th>
<th>Component name</th>
<th>Concentration, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Control</td>
</tr>
<tr>
<td>1</td>
<td>545</td>
<td>2-Methylpropanal</td>
<td>0.91</td>
</tr>
<tr>
<td>2</td>
<td>561</td>
<td>2-Methylpropanol</td>
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</tr>
<tr>
<td>3</td>
<td>570</td>
<td>2-Butanone</td>
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</tr>
<tr>
<td>4</td>
<td>579</td>
<td>Diacetyl</td>
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<td>5</td>
<td>588</td>
<td>2-Butanol</td>
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</tr>
<tr>
<td>6</td>
<td>597</td>
<td>Butanal</td>
<td>0.23</td>
</tr>
<tr>
<td>7</td>
<td>603</td>
<td>Ethyl acetate</td>
<td>0.53</td>
</tr>
<tr>
<td>8</td>
<td>607</td>
<td>2-Methylfuraran</td>
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<tr>
<td>9</td>
<td>615</td>
<td>2-Butenal</td>
<td>0.21</td>
</tr>
<tr>
<td>10</td>
<td>628</td>
<td>3-Methylbutanal</td>
<td>0.09</td>
</tr>
<tr>
<td>11</td>
<td>639</td>
<td>2-Methylbutanal</td>
<td>1.23</td>
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<tr>
<td>12</td>
<td>687</td>
<td>Pentanal</td>
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</tr>
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<td>13</td>
<td>718</td>
<td>2-Pentenal</td>
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</tr>
<tr>
<td>14</td>
<td>760</td>
<td>2-Methylpentanal</td>
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<tr>
<td>15</td>
<td>765</td>
<td>Butyric acid</td>
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<td>16</td>
<td>775</td>
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<td>17</td>
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<td>5-Methyl-2-hexanone</td>
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<td>18</td>
<td>831</td>
<td>Trans-2-hexenal</td>
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<tr>
<td>19</td>
<td>866</td>
<td>2-11 anone</td>
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<td>878</td>
<td>Heptanal</td>
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<td>21</td>
<td>913</td>
<td>5-Methyl-2-heptanone</td>
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<tr>
<td>22</td>
<td>926</td>
<td>α-Thujene</td>
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<tr>
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<td>932</td>
<td>α-Pinene</td>
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<tr>
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<td>1-Octen-3-ol</td>
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Table 3. Continued. Volatile compounds in fermented sausages

<table>
<thead>
<tr>
<th>№ of peak</th>
<th>Retention Index</th>
<th>Component name</th>
<th>Concentration, mg/kg</th>
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<tbody>
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<td></td>
<td></td>
<td></td>
<td>Control</td>
</tr>
<tr>
<td>29</td>
<td>999</td>
<td>α-Phellandrene</td>
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</tr>
<tr>
<td>30</td>
<td>1008</td>
<td>3-Carene</td>
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<tr>
<td>31</td>
<td>1011</td>
<td>α-Terpinene</td>
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<tr>
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<td>1014</td>
<td>p-Cymene</td>
<td>–</td>
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<td>33</td>
<td>1025</td>
<td>Limonene</td>
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</tr>
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<td>Ocmene</td>
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<tr>
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<td>1052</td>
<td>γ-Terpinene</td>
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</tr>
<tr>
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<td>m-Cresol</td>
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<td>1171</td>
<td>Methylguaiacol</td>
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<td>Methylchavicol</td>
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<tr>
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<td>1200</td>
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<td>52</td>
<td>1222</td>
<td>γ-Octalactone</td>
<td>0.26</td>
</tr>
<tr>
<td>53</td>
<td>1257</td>
<td>4-Ethylguaiaicol</td>
<td>0.92</td>
</tr>
<tr>
<td>54</td>
<td>1289</td>
<td>Undecanal</td>
<td>0.33</td>
</tr>
<tr>
<td>55</td>
<td>1293</td>
<td>2,4-Decadienal</td>
<td>0.05</td>
</tr>
<tr>
<td>56</td>
<td>1334</td>
<td>Eugenol</td>
<td>0.35</td>
</tr>
<tr>
<td>57</td>
<td>1341</td>
<td>Neryl acetate</td>
<td>0.12</td>
</tr>
<tr>
<td>58</td>
<td>1355</td>
<td>Decanoic acid</td>
<td>4.28</td>
</tr>
<tr>
<td>59</td>
<td>1378</td>
<td>Decanal</td>
<td>0.25</td>
</tr>
<tr>
<td>60</td>
<td>1387</td>
<td>β-Elemene</td>
<td>0.04</td>
</tr>
<tr>
<td>61</td>
<td>1400</td>
<td>Tetradecane</td>
<td>0.02</td>
</tr>
<tr>
<td>62</td>
<td>1426</td>
<td>Caryophyllene</td>
<td>0.38</td>
</tr>
<tr>
<td>63</td>
<td>1432</td>
<td>γ-Decalactone</td>
<td>–</td>
</tr>
<tr>
<td>64</td>
<td>1465</td>
<td>δ-Decalactone</td>
<td>0.05</td>
</tr>
<tr>
<td>65</td>
<td>1500</td>
<td>Pentadecane</td>
<td>0.10</td>
</tr>
<tr>
<td>66</td>
<td>1505</td>
<td>β-Selinene</td>
<td>–</td>
</tr>
<tr>
<td>67</td>
<td>1545</td>
<td>Dodecanoic acid</td>
<td>1.24</td>
</tr>
<tr>
<td>68</td>
<td>1559</td>
<td>Germacrren D</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Table 3. Ending. Volatile compounds in fermented sausages

<table>
<thead>
<tr>
<th>№ of peak</th>
<th>Retention Index</th>
<th>Component name</th>
<th>Concentration, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Control</td>
</tr>
<tr>
<td>69</td>
<td>1588</td>
<td>Tetradecalanal</td>
<td>–</td>
</tr>
<tr>
<td>70</td>
<td>1600</td>
<td>Hexadecane</td>
<td>0.12</td>
</tr>
<tr>
<td>71</td>
<td>1661</td>
<td>Bisabolol</td>
<td>0.11</td>
</tr>
<tr>
<td>72</td>
<td>1669</td>
<td>Farnesol</td>
<td>0.15</td>
</tr>
<tr>
<td>73</td>
<td>1682</td>
<td>Pentadecalanal</td>
<td>0.46</td>
</tr>
<tr>
<td>74</td>
<td>1700</td>
<td>Heptadecalane</td>
<td>0.30</td>
</tr>
<tr>
<td>75</td>
<td>1746</td>
<td>Tetradecanoic acid</td>
<td>4.79</td>
</tr>
<tr>
<td>76</td>
<td>1764</td>
<td>Phthalate</td>
<td>0.16</td>
</tr>
<tr>
<td>77</td>
<td>1777</td>
<td>Hexadecanal</td>
<td>0.09</td>
</tr>
<tr>
<td>78</td>
<td>1800</td>
<td>Octadecane</td>
<td>1.06</td>
</tr>
<tr>
<td>79</td>
<td>1900</td>
<td>Nonadecane</td>
<td>0.16</td>
</tr>
<tr>
<td>80</td>
<td>1924</td>
<td>Hexadecenoic acid</td>
<td>2.06</td>
</tr>
<tr>
<td>81</td>
<td>1948</td>
<td>Hexadecanoic acid</td>
<td>9.03</td>
</tr>
<tr>
<td>82</td>
<td>2000</td>
<td>Eicosane (Hydrocarbon - C20)</td>
<td>1.14</td>
</tr>
<tr>
<td>83</td>
<td>2118</td>
<td>Octadecanoic acid</td>
<td>3.64</td>
</tr>
<tr>
<td>84</td>
<td>2146</td>
<td>Octadecanoic acid</td>
<td>6.79</td>
</tr>
<tr>
<td>85</td>
<td>2175</td>
<td>Octadecadienoic acid</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 4. Percentage of volatile compounds in raw-cured sausages

<table>
<thead>
<tr>
<th>Samples</th>
<th>Class of compounds, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aldehyds</td>
</tr>
<tr>
<td>Control</td>
<td>6.06</td>
</tr>
<tr>
<td>P.shermanii + B.longum</td>
<td>9.06</td>
</tr>
</tbody>
</table>

Volatile compounds can be separated according to their possible origin. Spices could be responsible for the generation of terpenes and hydrocarbons. Phenols could be the components of smoke fume.

The study was shown that there is a significant difference in contents of volatile compounds between sausage samples. Their qualitative compositions are different. Some compounds were found only in experimental samples. For example, α-Thujene, p-Cymene, γ-Terpinene, Phenylethyl alcohol, γ-Decalactone, Tetradecanal, β-Selinene. These results could be related to different activities of starter cultures used in the study.

Carbonyl compounds (aldehydes, ketones etc.) play the main role in formation of aroma profile of meat products. The content of aldehydes in sausage with propionic-acid and bifidobacteria was 30% higher than with control sample. The content of ketones was 17% higher in experimental sample.

In addition, the content of phenols was two times higher in experimental sample than in control. It was stated the high contents of α-Phellandrene, 3-Carene, Methylguaiacol in this sample.

The contents of esters and carboxylic acids were nearly the same in both samples.

It is important to note the difference in terpene content between the sausage samples. The content of terpenes in experimental sample was 3.5-fold higher than in control sample (For example, the content of α-Pinene was 22-fold higher, the content of β-Myrcene
was 6-fold higher, the content of γ-Terpinene was 2-fold higher). α-Pinene has pines odour, β-Myrcene has pleasant smell, γ-Terpinene has lemon odour.

The main difference between the batches was in the content of lactones. It was tenfold higher in experimental sample than in control sample. The contents of δ-Decalactone and γ-Octalactone (both of them have sweet, coconut notes) were 10-fold higher in experimental sample. γ-Decalactone wasn’t found in the control sample, but was found in sample with experimental starter culture in concentration 7.77 mg/kg. The odour of γ-Decalactone can be characterized as sweet, fruity-peach and creamy.

It is well known fact that lactones are referred to uronic acids. For example, during fermentation of bifidobacteria D-glucose oxidizes with forming of D-glucuronic acid. The presence of lactones in experimental sample was the reason of mild creamy tone in sausage.

**REFERENCES**


**CONCLUSIONS**

The study demonstrated that sausages produced with *Propionibacterium shermanii* KM-186 and *Bifidobacterium longum* B379M as a starter culture contained several aroma-compounds that were not found in control samples. Also higher contents of terpenes, lactones, alcohols and phenols were found in sausages made with starter culture of propionic-acid bacteria and bifidobacteria compared to control samples. Results of sensory evaluation have shown that the experimental batch had better scores than the control batch. It indicates, that certain aroma compounds plays significant role in the formation of the aroma of raw-smoked sausages.

Thus, the finding of this study was to show that use of *Propionibacterium shermanii* KM-186 and *Bifidobacterium longum* B379M as starter cultures has positive influence on sensory characteristics of raw-smoked sausages.


INFLUENCE OF THE WHEY TYPE ON COMPOSITION AND PROPERTIES OF ITS MINERALIZATES

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Abstract: Physical and chemical properties of whey mineralizates obtained from unsalted cheese whey, curdy whey and casein whey treated by electrodialysis. The extent of electrodialysis treatment of whey on the structure of its dispersed phase was studied by the photon-correlation spectroscopy method. The considerable effect of electrodialysis treatment on the dispersed structure of whey, on stability of whey proteins that form the basis of the dispersed phase of whey was defined. These variations may significantly affect the organoleptic and technological properties of demineralized whey, its shelf life and biological value. It’s been established that the demineralization causes significant changes to the specific electrical conductivity and the active acidity of both whey and whey mineralizates. Their physical and chemical properties were studied with the following methods: potentiometry, conductometry, stalahmometric method, viscometry, refractometry. The elemental and phase composition were studied by a range of advanced methods, such as X-ray phase analysis, scanning electron microscopy, energy dispersive X-ray fluorescent microanalysis, infrared spectroscopy. It’s revealed that the main crystalline phases of whey mineralizates are the potassium and sodium chlorides, calcium and magnesium phosphates, calcium sulfate and carbonate. The results of infrared spectroscopy allowed identification of the lactate, citrate, sulfate and phosphate ions in the structure of whey mineralizates. The ultimate composition of whey mineralizates is represented by such chemical elements as Cl, Ca, Na, Mg, K, S, P, O, Al, Si and N. The correlation between the composition and properties of whey mineralizate and initial milk whey is established.

Keywords: Whey mineralizates, infrared spectroscopy, X-ray phase analysis, scanning electron microscopy, energy-dispersive microanalysis


INTRODUCTION

Electrodialysis treatment of whey is found to be the most effective method of targeted control of its mineral composition and acidity [1, 2]. It should be noted that the whey electrodialysis does not significantly affect the qualitative and quantitative properties of whey proteins, lactose content, and the content of vitamins in demineralized whey; in the meantime, its technological and organoleptic properties considerably improve [3].

The process of whey electrodialysis desalination or demineralization ends in demineralized whey and salt concentrate, namely, the whey mineralizate. The demineralized whey (especially when dry) is used in food production for children and for special purposes; in confectionery and bakery; for meat products; in pharmaceutical industry, etc. [1–5]. On the other hand, the whey mineralizates have not found the practical use. As shown in works [6, 7], whey mineralizates may be used as the basis for washing and disinfecting agents used in dairy enterprises. In this regard, the study of physical and chemical, surface-active properties and the composition of whey mineralizates, as well as the impact caused by the type of initial whey to such parameters are quite relevant.

OBJECTS AND METHODS OF THE STUDY

The targets of this research are the milk whey and whey mineralizates obtained by electrodialysis of unsalted cheese whey, curdy whey and casein whey. Milk whey was demineralized by the ED-mini electrodialysis device (manufactured by MEGA JSC, Czech Republic) using RALEXAMH-PES anion exchange membranes and RALEXSMH-PES cation exchange membranes. Samples were treated under the electrodialysis until 90% demineralization was achieved. Parameters of electrodialysis included the following: voltage \( U = 12.5 \) V; membrane area \( 0.14 \) m\(^2\); steam of membranes \( 10 \); diluate flow \( 70 \) l/h; temperature \( t = 22.0 \pm 2^\circ \)C. The volume of experimental whey mineralizates was produced at the International R&D “Electro-and Baromembrane Technologies” Laboratory of MEGAProfiLine LLC (Stavropol Territory, Stavropol).

The composition and properties of milk whey mineralizates were studied by laboratories of the Applied Biotechnology Department of the Institute of Living Systems and of the Department of Nanomaterial Technology of the Institute of Electric Power Engineering, Electronics and Nanotechnologies,
Federal State Autonomous University of Higher Education North-Caucasian Federal University, as well as by the R&D Laboratory "Physical Methods of Research and Analysis" of the Center for Collective Use of Scientific Equipment (Stavropol Territory, Stavropol).

The structure of the milk whey discontinuous phase was assessed by the photon-correlation spectroscopy method at the Photocor Complex unit (by Antek-97 LLC, Russia) [8]. The array of spectroscopic data was processed using the DynalS software. The method of conductivity measurements at the EXPERT-002 conductometer [9, 10] was applied to measure the specific conductivity (SC) of milk whey and its mineralizates. The active acidity of whey and mineralized whey was determined by potentiometric method; the density was measured by the hydrometer [11]; the limiting wetting angle was measured by the sessile drop method that is the direct measurement of the angle by the shape of a drop on the solid surface; the surface tension was measured by stalagmometric method [12]; the kinematic viscosity was measured by the glass capillary viscosimeter VPZh-1 (Technocom NPO, Russia) [13]; the refractive index was measured by the refractometer; the titrated acidity of whey mineralizates was determined by titrimetry as per the procedure [14]. The structure of mineralizates the availability of certain vibrations of atomic group bonds was determined by the infrared spectroscopy (IR spectroscopy) using the IR Fourier spectrometer of FSM 1201 model listed with the No. 18895-99 in the National Register of Measuring Equipment of Russia. The phase composition of dry residues of whey mineralizates was evaluated by X-ray phase analysis by the method of powder diffraction at the PANanalytical Empyrean X-ray diffractometer (manufactured by PANalytical BV, the Netherlands) as per the procedure [15]. The elemental composition of whey mineralizates dry residues was investigated using the energy-dispersive (elemental) analysis at the MIRA-LMH scanning electron microscope with the element determination system AztecEnergy StandardX-max 20 (standard) (manufactured by Tescan, Czech Republic) [16].

RESULTS AND DISCUSSION

Physical and chemical properties of whey and whey mineralizates were studied at the first stage. The process of milk whey electrodialysis allowed obtaining dependences of specific conductivity (SC) and active acidity of curdy whey, cheese whey, casein whey and whey mineralizates on demineralization level. The results are shown graphically below. Fig. 1 shows the dependence of the specific conductivity of milk whey on the degree of its demineralization.

As shown by the data analysis in Fig. 1, prior to the demineralization process, the initial milk whey had the values of specific conductivity as follow: the largest value obtained for the casein whey with SC = 9.54 ± 0.50 mS/cm, followed by the curdy whey with SC = 7.19 ± 0.55 mS/cm and the lowest value for the cheese whey with SC = 5.17 ± 0.52 mS/cm. The specific conductivity of all the whey samples studied in the process of electrodialysis treatment decreased on a straight-line basis. The process of demineralization of milk whey was completed as the specific conductivity value was reached of about 1–1.5 mS/cm that corresponded to 90% of demineralization.

Fig. 2 shows the dependence of specific conductivity of whey mineralizates on the extent of whey demineralization.

Analysis of dependencies shown in Fig. 2 shows that the specific electrical conductivity of whey mineralizates increases as the extent of whey demineralization rises due to ion transition entering the dispersion medium of milk whey and to the salt concentrate influenced by the electromotive force (EMF). Upon completion of electrodialysis treatment, the casein whey mineralize has the greatest specific conductance (SC) followed by the curdy and cheese whey that correlates with ion concentrations and SC of initial whey. In parallel with SC measurement, the active acidity (pH) was measured for both whey of various types and whey mineralizates. Fig. 3 shows the results of pH measurement of milk whey as it is demineralized.
It was found that the process of electrodialysis treatment results in the decrease of mineralizate active acidity of casein and curdy whey due to hydrochloric and lactic acid penetrated therein, respectively.

The active acidity of the cheese whey mineralizate varies insignificantly and is within 6 ≤ pH ≤ 7.5; this is apparently due to the order of ion passing to the mineralizate. It is possible that at the beginning of electrodialysis, the ions with acidic properties pass into the mineralizate to explain the decrease in pH, followed by ions of basic properties. At the end of electrodialysis treatment, the active acidity of mineralizes is within: in acidic area - for casein and curdy mineralizes (pH = 4.01 ± 0.21 and pH = 5.05 ± 0.22, respectively), in the slightly acidic area - for cheese mineralizate (pH = 5.92 ± 0.25).

Data were also obtained on the influence of extent of the whey electrodialysis treatment on the structure of its dispersed phase. The average hydrodynamic radius of particles of the dispersed phase was found by the photon correlation spectroscopy. Figure 5 shows the histogram of particle size distribution of the dispersed phase of initial curdy whey sample prior to electrodialysis treatment, distribution histograms of the dispersed phase particles for the cheese and casein wheys are similar.

The analysis of results indicates that curdy, cheese and casein whey samples have a single dispersed phase with the average hydrodynamic radius of about 130 ± 50 nm. Quite monodisperse distribution should be noted for the dispersed phase of milk whey by particle sizes.

The distribution histograms of the average hydrodynamic radius of particles of the dispersed phase of curdy, cheese and casein wheys at 90% demineralization are shown in Fig. 6 a, b, c.

---

**Fig. 3.** Dependence of the milk whey active acidity on the extent of its demineralization: (a) casein, (b) curdy, (c) cheese.

As per the analysis of dependencies shown Fig. 3, the active acidity values of tested whey species were as follow prior to demineralization: casein whey pH = 4.64 ± 0.11; curdy whey pH = 4.88 ± 0.12 and cheese whey pH = 6.86 ± 0.10. These active acidity values are well correlated with published data and are associated with processes to obtain these types of milk whey [2, 5]. For example, to produce the casein whey, the protein is coagulated using the hydrochloric acid (pH < 7), adding the HCl solution to the source milk until the isoelectric point of casein is reached (pH = 4.6) [17]. When producing curdy whey, the protein coagulation is associated with vital activity of lactic acid bacteria resulting in the large amount of lactic acid which is the weak electrolyte (pH < 7). The production of cheese whey is associated with the use of enzymatic processes that do not have a significant effect on acid-base properties of milk.

By the results of dependencies analysis as shown in Fig. 3, it was found that the active acidity of whey types tested decreases during demineralization. The greatest changes in whey pH are reported at the about 50% demineralization. This is apparently due to the process of water molecule decomposition on the membrane surfaces when this level of demineralization is reached under the effect of electric forces. This results in the release of the certain amount of H⁺ protons that determine the value of active acidity of the medium, and as a result, pH decreases. OH⁻ ions released during the water molecule decomposition have no significant effect on the whey active acidity as they are removed in process of further desalting, which may be related to the process technique due to the selective permeability of membranes used relative to hydroxide ions.

Fig. 4 shows dependences of whey mineralizate active acidity on the extent of whey demineralization.
Fig. 5. Histogram of distribution of hydrodynamic radii of particles of the curdy whey disperse phase.

Fig. 6. Distribution histograms of the hydrodynamic radii of particles of the whey dispersed phase at 90% demineralization: (a) curdy, (b) cheese, (c) casein.
As per the analysis of histograms shown in Fig. 6 a, b, c, at 90% demineralization the second fraction occurrence was reported in all three milk whey samples and its content in curdy and casein whey is significantly totaling over 50%; the content of the second fraction is about 5% in the cheese whey.

At the second stage of the study, data were obtained on physical and chemical properties of whey mineralizates as shown in Table 1.

The analysis of data shown in Table 1 indicates that values of such physical and chemical properties as density, wetting angle, surface tension, kinematic viscosity and refractive index are similar for all mineralizates tested and do not depend on the origin of raw stock. The active acidity of the medium, specific electrical conductivity and titratable acidity depend on the ionic composition of whey mineralizates and, in turn, they correlate with the ionic composition of the raw stock (curdy, cheese and casein whey).

At the third stage of the study, whey mineralizate samples were dried and tested by IR spectroscopy, X-ray phase analysis and scanning electron microscopy. Fig. 7 shows the IR spectra obtained.

As shown by the IR spectra explanation [18, 19] of dry residues of whey mineralizates, bands are seen in the area of valence vibrations that may be associated with -OH, -CH and -NH groups forming part of mineralizates [18, 19]; comprising mineralizates; the area of deformation vibrations is represented by bands typical for bonds present in lactate, citrate, sulfate and phosphate ions.

Due to the fact that certain compounds with ionic bonds comprising mineralizates are optically transparent in the IR spectrum area, the X-ray phase analysis was used to identify them and to define their structure. The resulting X-ray diffraction patterns are shown in Fig. 8.

As per the analysis of diffractograms, main phases of curdy, cheese and casein whey mineralizates are the potassium and sodium chlorides, as well as calcium and magnesium phosphates, calcium sulphate and carbonate. Main components of the crystalline phase of whey mineralizates are described in Table 2 [20].

### Table 1. Physical and chemical properties of whey mineralizates

<table>
<thead>
<tr>
<th>Type of initial milk whey</th>
<th>Active acidity of the medium, pH</th>
<th>Density, ρ, kg/m³</th>
<th>Wetting angle, θ, °</th>
<th>Surface tension, σ, mN/m</th>
<th>Titrable acidity, Т°</th>
<th>Kinematic viscosity, β, 10⁻⁶ m²/s</th>
<th>Refractive index, n</th>
<th>Specific conductivity, χ, mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curdy</td>
<td>5.05</td>
<td>1.005</td>
<td>96</td>
<td>76</td>
<td>16</td>
<td>0.904</td>
<td>1.334</td>
<td>7.16</td>
</tr>
<tr>
<td>Cheese</td>
<td>5.92</td>
<td>1.004</td>
<td>97</td>
<td>78</td>
<td>14</td>
<td>0.907</td>
<td>1.334</td>
<td>6.30</td>
</tr>
<tr>
<td>Casein</td>
<td>4.01</td>
<td>1.006</td>
<td>95</td>
<td>77</td>
<td>19</td>
<td>0.903</td>
<td>1.334</td>
<td>10.01</td>
</tr>
</tbody>
</table>

![Fig. 7. IR spectra of dry residues of whey mineralizates: (1) cheese whey, (2) curdy whey, (3) casein whey.](image-url)
Fig. 8. Diffractograms of dry residues of mineralizes of various whey: (a) cheese whey mineralizate; (b) curdy whey mineralizate; (c) casein whey mineralizate.
Table 2. Description of main components of the whey mineralizate crystalline phase

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Molecular mass</th>
<th>Type of crystal lattice</th>
<th>Space group</th>
<th>Elementary cell parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>74.5</td>
<td>Cubic</td>
<td>Fm-3m</td>
<td>$a = b = c (\AA):6.2917$ Alpha = Beta = Gamma ($^\circ$):90.0000</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>58.5</td>
<td>Cubic</td>
<td>Fm-3m</td>
<td>$a = b = c (\AA):5.6418$ Alpha = Beta = Gamma ($^\circ$):90.0000</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>CaCO$_3$</td>
<td>100</td>
<td>Orthorhombic</td>
<td>Pmcn</td>
<td>$a(\AA):4.9653$ b(\AA):8.0088 c(\AA):5.7847 Alpha = Beta = Gamma ($^\circ$):90.0000</td>
</tr>
<tr>
<td>Calcium orthophosphate</td>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>310</td>
<td>Orthorhombic</td>
<td>R3c</td>
<td>a (Å):10.3633 b(Å):10.3633 c (Å):37.2581 Alpha ($^\circ$):90.0000 Beta($^\circ$):90.0000 Gamma($^\circ$):120.0000</td>
</tr>
<tr>
<td>Magnesium orthophosphate</td>
<td>Mg$_3$(PO$_4$)$_2$</td>
<td>262</td>
<td>Triclinic</td>
<td>P-1</td>
<td>a (Å):8.5120 b(Å):8.9820 c (Å):9.3200 Alpha ($^\circ$):116.3400 Beta($^\circ$):91.5000 Gamma($^\circ$):114.4900</td>
</tr>
</tbody>
</table>

Whey mineralizate samples were tested by the scanning electron microscopy at the scanning electron microscope MIRA-LMH with the unit structure determination system AZtecEnergy Standart/X-max 20 (standard) by Tescan Company. Previously, the whey mineralizate sample elements were studied by the energy-dispersive microanalysis. The EDX spectra obtained are shown in Fig. 9.

Mathematical processing of EDX-spectra helps to specify components of whey mineralizates as shown in Table 3.

As per the analysis of data shown in Table 3, curdy, cheese and casein whey mineralizates contain such elements as Cl, Ca, Na, Mg, K, S, P, O, Al, Si (nitrogen (N) is also found in the cheese whey mineralizate). The highest content of Cl is found in the casein whey mineralizate due to the hydrochloric acid used to produce it. The content of Ca and P in mineralizates of curdy and casein whey is several times higher than in that of cheese whey. The reason is as follows: the calcium phosphate in the casein and curdy whey is mainly ionic and is easily removed treated by electrodialysis and easily passes into mineralizates; the calcium phosphate is colloidal in the cheese whey of pH ≈ 7, so it is hardly removed during electrodialysis. The content of K, Na, Mg, S in all milk whey mineralizates is fairly similar. In milk and whey, these elements form the ion-salt balance being not actively involved in colloidal system stabilization; these elements easily transform to mineralizate under the electrodialysis treatment of the milk whey.

It should be noted that it is not feasible to define the percentage of carbon by this method due to specific conditions for sampling, where a thin layer of carbon (5–10 nm) is applied onto the sample surface.
Fig. 9. EDX-spectrum of whey mineralizes: (a) cheese whey mineralizate; (b) curdy whey mineralizate; (c) casein whey mineralizate.
Table 3. Unit structure of milk whey mineralizates

<table>
<thead>
<tr>
<th>Unit</th>
<th>Content of elements in milk whey mineralizates, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>casein</td>
</tr>
<tr>
<td>N</td>
<td>–</td>
</tr>
<tr>
<td>O</td>
<td>45.76</td>
</tr>
<tr>
<td>Na</td>
<td>8.41</td>
</tr>
<tr>
<td>Mg</td>
<td>1.57</td>
</tr>
<tr>
<td>Al</td>
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</tr>
<tr>
<td>Si</td>
<td>0.09</td>
</tr>
<tr>
<td>P</td>
<td>6.13</td>
</tr>
<tr>
<td>S</td>
<td>1.20</td>
</tr>
<tr>
<td>Cl</td>
<td>15.79</td>
</tr>
<tr>
<td>K</td>
<td>9.92</td>
</tr>
<tr>
<td>Ca</td>
<td>11.06</td>
</tr>
</tbody>
</table>

Figures 10–12 show the test results of dry residues micro-structure of casein, cheese and curdy whey mineralizers obtained by scanning electron microscopy.

As per the analysis of SEM micro-images of whey mineralizate samples as shown in Figures 10–12, the microstructure strongly depends on the origin of the raw material, namely the whey. Polycrystalline formations of quite higher polydispersity are found in all milk whey mineralizates. The crystallite size in the casein whey mineralizate sample is 2 to 200 μm, of cubic shape that is relevant to the structure of potassium and sodium chlorides. Polycrystalline formations sized about 2 to 50 μm comprising of plates (“scales”) are found in samples of both cheese and curdy whey mineralizates.

Fig. 10. SEM micro-images of the dry residue of casein whey mineralizate.

Fig. 11. SEM-micro-images of the dry residue of the cheese whey mineralizate.
CONCLUSIONS

Resulting from studies above, we may conclude on the considerable impact of electrodialysis treatment on the dispersed composition of milk whey and, consequently, on the stability of whey proteins as the basis of the milk whey dispersed phase. These variations may significantly affect the organoleptic and technological properties of demineralized whey, its shelf life and bioavailability. The study of the impact of nature and ion concentration on the particle consolidation process of the milk whey dispersed phase remains urgent and requires further studies.

We can further conclude that the type of dairy raw material considerably impact the physical and chemical properties and structure of whey mineralizates.

ACKNOWLEDGEMENTS

The work was supported by the Ministry of Education and Science of the Russian Federation (Contract Minobrnauki of Russia № 2017-218-09-162).

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Fig. 12. SEM micro-images of the dry residue of curdy whey mineralizate.


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IMPACT OF BETA-LACTOglobulin HYDROLYSate ON STRUCTURAL AND MECHANICAL PROPERTIES OF ALLERGENIC POTENCY-RESTRICTED YOGURT

A. N. Ponomareva, E. I. Melnikova, E. V. Bogdanova, and D. V. Kharitonov

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Abstract: Creation and development of low-allergenic food products in sour-milk drink groups is the urgent trend in dairy industry development. By the results of patent search, one of challenging methods to reduce the dairy product allergenicity has been identified. To produce such products, the method involves using whey protein hydrolysates, in particular, β-lactoglobulin hydrolysate obtained by using enzyme preparations Flavorpro 750MDP and Promod 439L. The research aimed to study normalized milk mixtures fermented with β-lactoglobulin hydrolysate with the resulting changes in the chemical composition, as well as to select starter microorganisms that provide the required stability and structure of the milk coagulum by producing exopolysaccharides. The researches were carried out at the base of several laboratories as follow: The Federal Research Centre “Fundamentals of Biotechnology” of the Russian Academy of Sciences, Christian Hansen LLC, the Voronezh State University of Engineering Technologies and the Federal Research Centre of Nutrition and Biotechnology. This work is based on standard and conventional research methods. Advanced tools and information technologies were used to assess the properties of raw materials, semi-finished products and food products. By the results of studies completed, it was found unreasonable to replace over 20% of whole milk with β-lactoglobulin hydrolysate during normalization, since such replacement resulted in an increase in the mixture acidity and prevented the normal growth and development of Streptococcus thermophilus, the basic exopolysaccharide producer. At the same time, the length of fermentation increased up to 5–6 h as the mass fraction of β-lactoglobulin hydrolysate increased. The viscosity of the resulting coagulum increased due to the reaction of exopolysaccharides with the protein gel mesh and fixation thereof on the surface of protein matrix. The residual antigenicity of the finished product decreased to 48.5% relative to that of sour-milk drinks produced as per traditional technology.

Keywords: Low-allergy yogurt, β-lactoglobulin hydrolysate, starter microorganisms, exopolysaccharides, rheological behavior

DOI 10.21179/2308-4057-2017-1-41-50


INTRODUCTION

Currently, the sour-milk production, particularly production of beverages, is reported to develop at the rapid rates as compared to other dairy products [1], and to employ greater development challenges. This benefits from price affordability of this food category. In addition, the increase in output and consumption of sour-milk drinks is due to the widespread promotion of healthy food among the population.

These products are reported in the high content of essential amino acids (7–11 times higher than in fresh milk), magnesium salts, phosphorus, calcium, vitamins A, D, E that are involved in the human metabolism [2]. Organic acids and carbon dioxide have a strong stimulating effect on digestive glands, thereby improving the process of digestion and intestinal uptake. Sour-milk products enrich the gastrointestinal tract with lactic acid and other bacteria that can considerably increase the human immune activity, and some of them can also “settle down” in the intestinal tract [3]. These microorganisms are antagonists of pathogenic and opportunistic pathogenic microflora as well as of putrefactive bacteria in the human intestine. The calcium of fermented dairy products is easier digested since it transforms to a soluble state in the acid environment and it partially releases from protein molecules due to protein hydrolysis by starter microorganisms [4].

Currently, the Russian market of fermented drinks offers quite a wide range of products. However, of special importance are the development and integration of technologies to produce hypoallergenic and...
low-allergenic dairy products with the known reduced residual antigenicity that ensure immunological tolerance.

In our country, the product line of hypoallergenic and low-allergenic dairy products is limited to imported dry infant milk mixes [5]. In this sector, the integration of import substitution technologies is of great scientific and practical importance.

As per the data by the International Union of Immunological Societies, the known food-borne allergens in dairy products are the following: caseins, immunoglobulins, β-lactoglobulins, α-lactoalbumin, bovine serum albumin [6]. Hereat, as per the database by IUIS, BiPep, Allergen Online, AllerMatch, β-lactoglobulin is the most allergenic fraction [7, 8]. This is because the β-lactoglobulin is not hydrolyzed during ingestion affected by the pepsin (gastric juice enzyme) unlike other milk proteins. When proteins interact with cells of specific immunity in the human body, IgE and IgG are synthesized to different antigenic determinants of these proteins.

Various technologies are reported to ensure low-allergenic properties of dairy products as follow: isolation of protein substances using specific sorbents, physical effect on protein molecules, protein proteolysis affected by enzyme preparations [9]. It results in conformational transitions in protein molecules causing changes in the structure and digestibility of denatured proteins, as well as the destruction or access restriction to antigenic epitopes [10, 11].

The most challenging approach to reduce the allergenicity of dairy products is the biocatalytic conversion of milk proteins focused on obtaining hydrolysates thereof with specified molecular mass distribution and residual antigenicity. The specificity of proteolytic enzymes with respect to the type of peptide bond is one of the main properties of such systems that allow obtaining food products of various level of protein hydrolysis. The use of enzymatic hydrolysates as a protein component of specialized products is aimed at reducing or eliminating the milk protein allergenicity and concurrent eliminating the risk of the body sensitization. In addition, hydrolysed proteins are reported to have certain physiological effect on the human body resulting from the accelerated indigestion process of short-chain peptides in the intestinal tract as compared with native proteins and amino acids [12].

To obtain the yogurt with the reduced residual antigenicity, we proposed to use β-lactoglobulin hydrolysate developed using enzymatic preparations Flavorpro 750MDP and Promod 439L [13]. It is a source of functional ingredients as follow: protein (3.18%, including the pure protein 1.17%), lactose (4.5%), calcium (84 mg%), phosphor (157 mg%), magnesium (10 mg%), potassium (102 mg%), retinol (0.03 mg%), tocopherol (0.03 mg%), Vitamin C (1.17 mg%), pyridoxine (0.07 mg%), riboflavin (0.14 mg %), thiamine (0.035 mg%), vitamin PP (0.05 mg%) [14]. As components of the β-lactoglobulin hydrolysate, calcium and phosphor are at the ratio best effective for indigestion, where the balanced content of essential aminoacids ensures its high biological value and digestibility. The biofunctional properties studied in vitro and in vivo proved that resulting from the cheese whey bioconversion, the hydrolysate obtained is described to have the antioxidant, hypolipidemic and hypocholesteremic action.

The specific whey flavor of the hydrolysate may be eliminated by the lactic acid fermentation since lactic acid microorganisms are known for their ability to use certain amino acids and peptides as a source of nitrogen for their metabolic needs. This accelerates the fermentation process and avoids the potential bitter taste of the finished product.

The proportioning of the normalized formula and the β-lactoglobulin hydrolysate was of great importance when developing the formulation since hydrolysis products (peptides, amino acids) are known for their bitterness. Challenging was to ensure a decrease in antigenicity and acceptable organoleptic properties of the sour-milk drink obtained. To this end, the feasibility to introduce various mass fractions of β-lactoglobulin hydrolysate to normalized mixtures was studied (Table 1). The change in the ratio of casein to whey proteins in the normalized formula resulting from β-lactoglobulin hydrolysate available in the formulation may cause a decrease in the ability of the mixture to acid gelation due to different spatial structure of molecules [15].

Monomeric casein components are associated in submicelles resulting from the hydrophobic and weak electrostatic interaction, and also due to the formation of phosphate-calcium bridges. The high content of proline uniformly distributed over the surface of casein micelles prevents the formation of the compact globular structure. The decrease in the surface potential results in reduction of the thickness of micelles hydrated shell and the strength of their intermicellar repulsion. When the isoelectric point is attained, the micelles are associated with gel formation or casein coagulation.

Table 1. Ratio of formulation ingredients in normalized formulas studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>Milk mix / β-lactoglobulin hydrolysate, %</th>
<th>Mass fraction of β-lactoglobulin hydrolysate, %</th>
<th>Weight ratio, % of total protein, %</th>
<th>Mass fraction of pure protein, %</th>
<th>Ratio casein/serum proteins/peptides + free amino acids</th>
<th>Mass fraction of lactose, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>100/0</td>
<td>0.33</td>
<td>3.2</td>
<td>3.17</td>
<td>88/10/2</td>
<td>4.70</td>
</tr>
<tr>
<td>1</td>
<td>90 : 10</td>
<td>0.29</td>
<td>3.2</td>
<td>3.06</td>
<td>80/11/9</td>
<td>4.72</td>
</tr>
<tr>
<td>2</td>
<td>80 : 20</td>
<td>0.25</td>
<td>3.2</td>
<td>2.93</td>
<td>73/12/15</td>
<td>4.74</td>
</tr>
<tr>
<td>3</td>
<td>70 : 30</td>
<td>0.22</td>
<td>3.2</td>
<td>2.72</td>
<td>65/13/22</td>
<td>4.76</td>
</tr>
</tbody>
</table>
Serum proteins are known for the compact structure of spherical or ellipsoidal shape. Intramolecular disulfide bridges stabilize the folds of the polypeptide chain. Hydrophobic side chains are inside the molecules where polar and electrically charged groups are found on the surface that forms the hydrated shell with the help of hydrogen bonds. Electric charges are uniformly distributed over the surface with low total value thereof. These molecules form the hydrophilic sol that does not precipitate at the isoelectric point, and coagulates when the larger amount of electrolyte is added. Due to that, caseins coagulate at the isoelectric point unlike serum proteins that remain in the serum as dissolved [16].

For sour-milk drinks, the strength of the gel obtained is the quality parameter. It depends on the structure of aggregates formed, including on the strength and location of casein fibers, dimensions of cavities in the gel mesh. Gels with larger cells of the spatial structure are more delicate, too sensitive to physical impact where the presence of large capillaries facilitates the retention of water by these gels. The excess content of denatured β-lactoglobulin bound to κ-casein prevents the heavier association of casein particles during the gel structure formation.

Since β-lactoglobulin hydrolysate added in the course of normalization process results in considerable changes in the ratio of casein/whey proteins/peptides and free amino acids, as well as in an increase in the lactose mass fraction in the mixture, the research aimed at studying the fermentation of normalized mixtures with β-lactoglobulin hydrolysate in view of the ability of starter microorganisms to synthesize exopolysaccharides (EPS) and to participate in the formation of structural and mechanical properties of the finished product. EPSs are known for the certain physiological effect. The availability of these substances increases the time for the consumed product to be ingested in the gastrointestinal tract that may be useful for the short-term colonization of probiotic bacteria.

OBJECTS AND METHODS OF STUDY

Research objects are the normalized formulas with β-lactoglobulin hydrolysate obtained by using enzyme preparations Flavorpro 750MDP and Promod 439L (STO 00426012-005-2014) [11] and the yogurt based on them.

Pilot studies were conducted at the base of The Federal Research Centre “Fundamentals of Biotechnology” of the Russian Academy of Sciences, Christian Hansen LLC, the Voronezh State University of Engineering Technologies and the Federal Research Centre ofNutrition and Biotechnology (Russian Federation).

Research methods are standard and common for research practice, as well as modified, improved and specific implemented by using the advanced equipment and information technologies to assess properties of raw materials, semi-finished products and food products.

To isolate EPSs from the resulting sour-milk coagulum, pronase and sodium azide were used. The enzymatic reaction was blocked by boiling followed by centrifugation to separate germ cells and proteins. EPS was coagulated by adding ethanol and sodium chloride solution at the concentration of 5 mol/dm³ to the supernatant. Prior to the test, the EPS was dissolved in the distilled water. The EPS concentration in the resulting solution was determined by the colorimetric phenol-acid method [17]. As a standard substance, glucose was used.

The structural and mechanical properties of yogurts were evaluated using the Brookfield RVDV-II + Pro rotary viscometer (USA). The mechanical stress was determined as the function of shear rate. The mechanical shear was established by the time of increase or decrease in the shear rate. The study results were evaluated by the deflection curve used to calculate the apparent (effective) viscosity at different shear rates, as well as hysteresis (cyclic zone between the upper and lower curve).

The impact of the mass fraction of β-lactoglobulin hydrolysate added and the type of starter culture used on the viscosity of the finished product was evaluated upon the fermentation of the normalized mixture for 5–6 hours at the temperature of (40 ± 2)°C [18, 19].

The experimental study results have been processed using the method of mathematical statistics as the data of various experiments were evaluated in triple sequence. Calculations, plotting and description thereof were supported by the Brookfield Rheocalc32 software and Microsoft Office 13 Application for Windows 8. The MathCad 16.0 application software package was used for graphical interpretations and data processing. The results obtained are known for high reproducibility, mutual consistency of test values and the correct statistical processing.

The study results were validated under factory conditions at the PJSC Dairy Plant “Voronezhsky” (Voronezh, Russian Federation).

RESULTS AND DISCUSSION

In compliance with the technical regulations of the Customs Union “On safety of milk and dairy products” TR TS 033/2013, a mixture of strains of Lactobacillus bulgaricus and Streptococcus thermophilus is used to produce the product line of yogurt [20].

As the strains are added to the normalized milk, they rapidly multiply since the mixture acidity furthers their growth. At the initial stage, they use free amino acids of milk to synthesize proteins and enzymes in the course of their activity the amount of which decreases during the first hours of culturing. Further on, the proteolytic decomposition of milk proteins occurs when exoenzymes of bacterial cells are generated. Concurrently, to obtain the right volume of energy, lactose is fermented by lactic-acid bacterium to form the lactic acid [21]. As they multiply, the lactic acid intensely accumulates, the medium pH decreases and at pH = (4.6–4.7) the milk proceeds to gel formation.

The lactic acid formation determines the process of protein coagulum formation to define the consistency of the finished product. It adds some pleasant and sourish flavor to the yogurt, and its content depends on the composition of the normalized formula, the
composition of the bacterial starter and process parameters. It is known that when mixed cultures of lactic microorganisms are used, the rate of acid formation is higher than separate strains are used [21]. This is due to the fact that resulting from the symbiosis, the cultures known for weak proteolytic activity (for example, Str. Thermophilus) are stimulated by cultures with higher activity (Lbm. Bulgaricus) that ensures an increase in the overall degree of protein hydrolysis. Therefore, the possibility to use the formula of various starter cultures has been studied to produce the high quality yogurt. When selecting strains of microorganisms the following factors were considered:
- maximum dynamics of acid formation during fermentation in the medium with high content of free amino acids;
- high capacity of starter cultures to synthesize exopolysaccharides that compact the product consistency by binding unbound moisture and slowing the serum separation.

EPSs are the carbohydrates of high molecular weight consisting of repeated residues of monosaccharides. The concentration of EPS found in fermented milk products usually ranges from 50 to 600 mg/dm³ depending on the culture and fermentation conditions. The amount of EPS is also dependent on the structure of the growth medium, especially the presence of carbon and nitrogen sources [22]. The ability to produce EPSs is common among some lactic bacteria, in particular, in some strains of S. thermophilus, Lb. Bulgaricus and Lactococcus lactis subsp. cremoris that are widely used in production of sour-milk drinks.

The EPS bio-synthesis may be divided in two stages: The first stage is the central carbohydrate metabolism when precursors of nucleotide sugars are formed. On the second stage, nucleotide sugars are combined to form the oligosaccharide repeating unit that polymerizes and is released. These stages are encoded in genes in the EPS gene cluster, for example, in the chromosome of S. thermophilus. The production of EPS is unstable, they may break down when cultivating microorganisms. This may result in the loss of plasmids in their cells as a result of mobile genetic elements emergence or DNA erasure, as well as of DNA rearrangement [22].

The milk gel containing EPS is the mixture of bio-polymer proteins and EPS along with other components. The properties of this mixture depend on whether the bio-polymers are segregational at certain concentration (thermodynamically incompatible, resulting in aggregation of molecules of the similar type or in phase separation), compatible (coexisting in solution) or associative (capable of complex aggregation) [22, 23]. In this case, their charge is important since it is known that direct interaction can occur between negatively charged EPS and the protein structure only. This makes it possible to obtain the protein coagulum of high gloss and viscosity and of low degree of strength and syneresis.

The reason of syneresis may be the casein particle restructuring in the gel structure and the degree of dissolution of the colloidal calcium phosphate during the coagulum formation. The protein structure compression, as well as the internal pressure of the coagulum and protein sedimentation during storage may also cause the syneresis. This phenomenon results in the reduction in the shelf life of fermented milk products, so it is undesirable for the process cycle.

It is established that the maximum volume of EPSs was produced by cultures fermented by F-DVS YF-LX700 (Fig. 1). This sample of yogurt was known for its high viscosity, low syneresis and higher resistance to stirring. The reduction in serum separation in the finished product is due to resulting EPSs that further bind the protein mesh encasing the serum by its strands. The syneresis prevention is directly proportional to the EPS concentration (the higher is the EPS content, the better is the encapsulation).

All the samples studied may be classified as pseudo-plastic rheological objects described by the Ostwald equation and are known for their coagulation-condensation structure [24]. Their response to the applied deformation varied depending on the shear rate. The presented rheological curves describe the properties of structured systems that characterizes intermolecular interaction between the EPS and the protein coagulum in all fermented drinks. Hereat, the plastic flow of milk gels and disproportionate dependence between the shear rate and internal stress in samples were noted. The transition of tested samples to the state of spreadable flow upon application of the constant load resulted in stabilization of viscosity values of mixtures corresponding to the horizontal section of curves. The tested food systems had stable structures. As the shear rate increased, the viscosity of samples reduced to be explained by the breakdown of the protein coagulum structure. The maximum values of critical shear stress were reported in drinks produced by using starters F-DVS YF-LX700 and F-DVS YoFlex Harmony 1.0 (Fig. 2).

It was found that an increase in the mass fraction of β-lactoglobulin hydrolysate in the normalized mixture resulted in the decrease in the critical shear stress of yogurt samples (Fig. 3). An inverse relationship between the viscosity and stability of the resulting milk gel was reported. The concept of stability includes the values of elastic and viscous modulus, depends on the length of load application and is the qualitative parameter of organoleptic yogurts properties.

Studies have been conducted to change rheological properties of yogurt samples produced by using fermentation starters F-DVS YF-LX700 and the control sample (Str. thermophilus and Lbm. delbrueckii subsp. bulgaricus) upon the destruction (loading) and subsequent reconstitution (unloading) of the structure (Fig. 4). During the stress phase in sour-milk drinks, the reversible structural decomposition occurred resulting in the decrease in the sample viscosity. During the phase of discharge, the structure of tested samples partially reconstituted.
Fig. 1. Content of EPS in yogurt samples.

Fig. 2. *Beginning*. Graphic expression of the dependence of critical shear stress on the shear rate of yogurt samples: (a) no. 1; (b) no. 2; (c) no. 3; (d) of control sample.
Fig. 2. Ending. Graphic expression of the dependence of critical shear stress on the shear rate of yogurt samples: (a) no. 1; (b) no. 2; (c) no. 3; (d) of control sample.

Fig. 3. Effective dynamic viscosity of yogurt samples (at the share rate of 300 s\(^{-1}\)).
Fig. 4. Graphic expression of the dependence of critical shear stress on the shear rate of yogurt samples: (a) no. 1; (b) no. 2; (c) no. 3; (d) of control sample.
The area of the hysteresis loop (as a percentage of area under the upper curve) is not a direct physical parameter of viscosity. However, the high level of hysteresis in yogurts containing EPS means that these products are less able to reconstruct the structure upon the failure by shear. The structure of the sour-milk drink partially breaks down in the rheometer and in the mouth when having meal. Thus, in case of shear, EPS are likely to be redistributed into large clusters into the intermediate continuous phase and surrounded by acidified casein helium particles obtained by breaking the initial gel. As a result of thermodynamic incompatibility between the casein and EPS, the intermediate phase slows the protein fragment reassociation. Therefore, yogurts containing EPS are reported to have a higher level of hysteresis with respect to the product obtained by using the traditional technology.

Thus, it is established that an increase in the mass fraction of β-lactoglobulin hydrolysate, and accordingly, in the mass fraction of free amino acids in the normalized mixture will promote an increase in the rate of starter microorganism growth. This is due to the fact that a larger number of amino acids are required for the life of lactic bacteria and the thermophilic streptococcus is known to have the maximum need for this growth factor [21].

However, by the results of studies completed, it was found unreasonable to replace over 20% of whole milk with β-lactoglobulin hydrolysate during normalization, since such replacement resulted in a decrease in the mixture acidity and prevented the normal growth and development of Streptococcus thermophilus, the basic exopolysaccharide producer. This may be explained by that the optimum of enzyme action triggered by the yogurt ferment varies within pH = (5.7–6.0), and at pH below 5.0 their activity reduces for 50% [21]. At the same time, the length of fermentation increased up to 5–6 h as the mass fraction of β-lactoglobulin hydrolysate increased. The viscosity of the resulting coagulum increased due to the reaction of exopolysaccharides with the protein gel mesh and fixation thereof on the surface of protein matrix.

Based on researches conducted, the component formulation for the low-allergenic yogurt was developed providing for 20% replacement of the normalized milk mixture with β-lactoglobulin hydrolysate, elimination of the stabilizer as compared with the control sample and the reduction of the residual antigenicity of the finished product to 48.5% relative to the sour-milk drinks produced by standard technology.

To validate low-allergenic properties of the yogurt obtained, its clinical and physiological properties were evaluated at the Allergology Department of the Federal Research Centre of Nutrition and Biotechnology. By the results of clinical chemical and immunological studies it has been established that the content of high-molecular protein structures does not exceed 57.5% of the total protein-peptide material, and not more than 44.4% of peptide-amino acid structures of the molecular masses less than 11.3 kDa.

Daily consumption of the yogurt obtained for 14 days by patients with known alimentary allergy did not result in changes in the level of serum concentration of total protein and circulating IgG and IgE antibodies specific for β-lactoglobulin. When the test product was added to the patients’ diet, there was no statistically significant changes in the serum concentration of TBA-reactive products, as well as changes in the anion-exchange capacity of blood serum of patients relative to the peroxy radical. This indicates that the lipid peroxidation is prohibited due to the high concentration of peptides with antioxidant properties in the finished product.

In compliance with the report by Federal Research Centre of Nutrition and Biotechnology, the sour-milk drink obtained was classified as the dietary (preventive) food product for children over 3 years of age with the known alimentary allergy to milk proteins.

The physical and chemical and microbiological properties of the finished product met requirements of TR TS No. 027/2012 "On safety of certain types of specialized food products, including dietary health food and dietary preventive nutrition", and TR TS No. 033/2013 "On safety of milk and dairy products". The low-allergenic yogurt was reported to have the mass fraction of physiologically functional ingredients, including vitamins, so it may be classified as the food of the functional product group.

Based on the study of microbiological, physical and chemical properties of the developed sour-milk drink during its storage, it has been established that its shelf life is no longer than 14 days at the temperature of 4 ± 2°C and the relative humidity of not more than 83%.

To produce the new sour-milk drink, the standard scheme was taken as the basis that specifies the use of additional operations to obtain the β-lactoglobulin hydrolysate. Due to application of commercially available equipment, the presented process scheme does not complicate the production process.

This process scheme is adapted to the HACCP system: the temperature, time intervals of temperature influence and residual antigenicity were taken as critical control points using the “decision tree” method. The application of this scheme in the technological process will ensure high quality, reduction of residual antigenicity, sanitary and hygienic safety, biological value and stability of properties of the finished product.

The technical documentation (TU 9222-512-00419785-13 “Lactic food products for dietary preventive nutrition”) was developed and approved, and the state registration certificate was obtained for the yogurt with the reduced allergenicity.

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FORMATION AND STUDY OF SYMBIOTIC CONSORTIUM OF LACTOBACILLI TO RECEIVE A DIRECT APPLICATION STARTER

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Abstract: One of the ways of formation of innovative products is the design of new types of direct application starters on the basis of viable microorganisms for their further use in the dairy industry. The purpose of the study was the isolation of lactobacilli activators of lactic fermentation made of national Kazakh drinks (ayran, koumiss, chegen and kurunga) for the formation of symbiotic consortium to receive a direct application starter. The authors have isolated and studied the following strains of microorganisms: Lactobacillus delbrueckii subsp. bulgaricus, Lactobacillus acidophilus, Streptococcus thermophiles, Lactococcus lactis subsp. lactis, Lactococcus lactis subsp. lactis biovar diacetilactis, Lactobacillus paracasei, Lactobacillus fermentum, Pediococcus damnosus, Pediococcus acidilactici, Lactobacillus gallinarum. Cultural, morphological and physiological and biochemical properties have been studied, the antibiotic resistance, antagonistic activity and biocompatibility of the isolated microorganisms have been determined. It has been established that the isolated microorganisms have a stick-like shape of 0.6 x 3.5 to 6.0 x 0.7 microns in size characteristic of the sort Lactobacillus bacteria, and are Gram-positive and nonspore-forming. Mobility was only observed in the strains Lactococcus lactis subsp. lactis biovar diacetilactis, Pediococcus damnosus and Pediococcus acidilactici. The strains differed considerably from each other by the consumption of other carbohydrates, however all the studied strains ferment ribose, D-galactose, D-glucose, D-fructose, D-mannose, N-acetyl-glucosamin, amygdalin, aesculin, salicine, cellobiose, maltose, lactose, D-sucrose which is characteristic of the representatives of the sort Lactobacillus. All the studied strains are sensitive to the effect of β-laktam antibiotics except Streptococcus thermophiles. The analysis of biocompatibility has shown that full compatibility is only characteristic of four strains – Lactobacillus gallinarum (kurunga), Streptococcus thermophilus (koumiss), Lactococcus lactis subsp. lactis (ayran) and Pediococcus damnosus (chegen). To create a symbiotic consortium such strains of microorganisms as Lactobacillus gallinarum, Streptococcus thermophilus, Lactococcus lactis subsp. lactis and Pediococcus damnosus and optimum conditions of cultivation have been chosen. The maximum growth of microorganisms has been noted in the following culture medium: proteose-peptone – 5.00; meat extract – 10.00; yeast extract – 5.00; glucose – 20.00; Tween-80 – 1.00; ammonium citrate – 1.00; manganese sulfate – 0.05; sodium hydrophosphate – 1.00; agar-agar – 15.00; methyl rosaniline – 0.0002; casein hydrolyzate – 12.50; papain digest of soy flour 2.50; sodium chloride – 3.00; sodium citrate – 0.50; sodium sulfite – 0.20; L-cystine – 0.05; sodium azide – 0.10; potassium phosphate dibasic – 0.50; ammonium citrate dibasic – 0.80.

Keywords: Consortium of microorganisms, lactobacilli, dairy products, microorganism isolation, direct application starter, antagonistic properties, antibiotic resistance, identification of microorganisms, symbiotic systems


INTRODUCTION

The problems of production and consumption of dairy products become more and more relevant and increasingly dependent on the general tendencies of development of the world food market [1]. Changes in the development of dairy business which are already determined by the processes of globalization of the world economy, the changes of the social food patterns of the population which are reflected in the structure of agrofood markets, the growth of level of information and technical support, the deterioration in the ecological situation and the achievements of world science in the field [1, 2] can already be observed in practice.

According to experts, only 8–12% of the health of a nation depend on the health system while the percentage of influence on the health of social and economic conditions and mode of living is 52–55%, at the same time one of the main components is the food factor [3, 4].

Improper feeding is the frequent reason of the development of malfunction of a lot of organs and

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systems. It is possible to influence metabolism and the adaptive and compensatory abilities of an organism by changing feeding habits. Now the developments of healthy food products that meet the evidence-based recommendations about the balanced diet of the population [4] are being performed. The main orientation of these studies is the improvement of metabolism and the increase in the immune properties of an organism by the correction of the protein, fat and carbohydrate component of the product.

Sour-milk products make a sizable group of healthy food products. The useful properties of sour-milk products are, first of all, that they improve metabolism, stimulate the exudation of gastrointestinal juice and are the source of highly digestible calcium. The presence of the microorganisms in their structure capable to survive in intestines and to supress putrefactive microflora provides the inhibition of putrefactive processes and the termination of formation of poisonous proteolysis products flowing into human blood [5, 6].

Starters are pure cultures or the mix of pure cultures of the lactic bacteria added into milk to obtain high-quality sour-milk products by means of lactic and spirit fermentation.

Starters consisting of different strains and often of different types and sorts of microorganisms, as well, are applied to produce sour-milk products [7]. It allows to improve the starter resistant to adverse effects [8].

Starters are usually prepared on the basis of monocultures or of the mechanical mix of several strains. The most often applied lactobacilli which are the causative agents of lactic fermentation are: Lactobacillus delbrueckii, Lactobacillus acidophilus, Lactobacillus bulgaricus, Lactobacillus plantarum, Lactobacillus brevis and Lactobacillus helveticus [9, 10].

However such starter cultures are often insufficiently effective. The abstract concepts allow to believe that it is preferable to use symbiotic cultures of microorganisms. The elaboration of combined direct starters is due to a new approach – the creation of the artificial symbiotic systems that have a wide range of necessary characteristics [11].

In this regard, the development of the evidence-based approaches based on the study of physiological and biochemical and industrially valuable properties of lactic microorganisms of various groups is relevant when making combined starters of direct application with a high activity.

The purpose of the work is the formation and study of symbiotic consortium of lactobacilli to obtain a direct application starter.

**OBJECTS AND METHODS OF STUDY**

The strains of microorganisms isolated from national Kazakh drinks became the object of scientific research:

- ayran in accordance with GOST 31702-2013 [12];
- koumiss in accordance with GOST R 52974-2008 [13];
- chegen (imported);
- kurunga in accordance with GOST 10382-85 [14].

The isolation of microorganisms from national Kazakh drinks was performed as follows: 1 ml of each of sour-milk drinks (ayran, kurunga, koumiss and chegen) was taken, culture media were added and plates and test tubes were incubated statically at a temperature of 37°C in a carbon dioxide medium for 1–5 days.

For primary isolation a lactic medium – sterile skim milk; MRS broth, brain heart infusion broth; milk agar – milk with agar of 3% in the ratio of 1 : 1; fish peptone agar and MRS agar were used.

Exhaustive sowings with the use of plates were performed from the test tubes with the visible growth of microorganisms (turbidity or the presence of a dairy clot) and from the combined lawns. The isolated microorganisms were cultivated on the agarized media (fish peptone agar, MRS agar and milk agar), cloned to pure cultures and their genetic identification and the analysis of antimicrobic properties were performed.

The study of phenotypical and morphological properties of microorganisms was performed in a dense medium – MRS agar, g/l: bacto-peptone – 10.0; meat extract – 10.0; yeast extract – 5.0; glucose – 20.0; Tween – 1.0; ammonium citrate – 2.0; sodium acetate – 5.0; sodium hydrophosphate – 2.0; magnesium sulphate 7-water – 0.1; manganese sulfate 5-water – 0.05; agar – 20.0.

In the course of study the diameter of colonies, color, their form, consistence, structure, surface and edge pattern were determined.

The main method to study the morphology of bacteria is the microscopy of the fixed stained medicines. The microscopic examination was performed with the use of the biological microscope Axio Scope A1 (“Carl Zeiss”, Germany). The determination of sizes of cells of the studied cultures of microorganisms was performed with the use of an ocular ruler and an object micrometer.

The differentiation of bacteria by the biochemical properties of their cellular wall was performed according to Gram with the use of a set for Gram staining (“Lab-Biomed”, Moscow). The essence of the method is that the cellular wall of Gram-positive bacteria tightly fixes gentian violet, does not become colourless after using ethanol and therefore does not perceive additional dye (fuchsin). Gentian violet is easily washed away by ethanol from the cell in Gram-negative microbes, and they are stained by additional dye.

The staining of bacteria spores was performed according to Schäffer-Fulton. The essence of the method is the combined effect of concentrated solution of ethyl green dye and temperature on the low-permeable spore exine with the further decoloration of cytoplasm of a vegetative cell and its contrast finishing dyeing using safranin. Spores are stained in green and cells in red during the microscopic examination.

The existence of flagella is established by the study of cultures for vagility in “the crushed drop” medicines.

The determination of physiological and biochemical properties of strains of microorganisms was performed with the use of microtests – the API-50
test systems (Promix, Russia) or the indicator paper systems which are a set of plastic holes with indicators.

The antibiotic resistance of the considered lactic bacteria was analyzed by means of a set of the disks impregnated with different types of antibiotics. The antibiotic disks were plated on a dense culture medium sowed by the culture of the studied strain and were cultivated for a day at a temperature of 37°C. Then the diameter of inhibition zone around the disks was measured.

The antagonistic activity was studied with the use of the following test strains: Escherichia coli B-6954, Bacillus fastidiosus B-5651, Pseudomonas fluorescens B-3502, Pseudomonas aeruginosa ATCC 9027, Leuconostoc mesenteroides B-8404, Candida albicans ATCC 885-653 and Staphylococcus aureus ATCC 25923 based on a dense culture medium using a diffusive method. In this regard, the test strain was plated on an agarized culture medium (fish peptone agar) in the form of lawn and the lawn at the same time was covered with the paper discs impregnated with lactobacillus metabolites (10 µl per disc). A disk with the MRS medium was used as a control sample, and disks with the antibiotics ciprofloxacin and gentamycin from a standard set were used as comparison medicines. The plates were incubated at 37°C for 24 hours. The results were taken into account by the presence and size (in mm) of the transparent zone of non-growth of microorganisms around the disc.

The study of biocompatibility of microorganisms was performed using the method of co-culture on a dense MRS culture medium. The diurnal culture grown up on a liquid culture medium and standardized according to the standard of turbidity was put on the surface of dense culture medium in the form of a bacteriological loop with a diameter of 3 mm. A drop of other tested culture which covered approximately half of the first drop when spreading was put on the surface of the same medium with the same volume after the absorption of the drop, having receded 1–2 mm from its edge.

In the superimposed part the cultures develop with a mutual presence (co-culture) competing with each other. After drying of the second drop the plate with crops was turned upside down and incubated at 28–32°C in the air medium. Each experiment was made with two repetitions, changing the position of cultures (to exclude the influence of sequence of stratification of drops of cultures on the nature of growth in the co-culture zone). The drops of the same culture layered on each other according to the technique described above were the control sample.

The account of results was performed in 24 and 48 h after the beginning of incubation. With the growth inhibition of one of the studied cultures the relations between them were considered as antagonistic, and the cultures themselves were assigned to the category of bioincompatible ones. The cultures were considered biocompatible in case of revelation of full merge of spots or an increase in the growth of the studied strains in the co-culture zone (mutualism, synergism and satellism). If one of the cultures goes upward in the co-culture zone suppressing the growth of the second culture irrespective of the sequence of their application, such a variant was regarded as poor antagonism. The existence of a distinct oppression (growth inhibition) zone of one culture along the periphery of stain of the other tested culture was regarded as a sign of high antagonism.

The choice of optimum composition of culture medium for the cultivation of consortium of microorganisms was performed by means of variation of the ratio of components and the assessment of viability of consortium of microorganisms. The cultivation was performed at a temperature of 37.0 ± 2.0°C, with the active acidity of 6.8 ± 0.2 and duration of 24 h.

### RESULTS AND DISCUSSION

Table 1 provides the pure cultures of microorganisms isolated from dairy drinks.

The morphological properties of microorganisms are studied in stained medicines for the purpose of their differentiation, analyzing their geometry, size, Gram staining, the existence of spores, capsules and flagella [15]. The shape and size of spores, capsules and flagella are influenced by the composition of culture medium and the cultural variability of microorganisms [16].

Table 2 provides the results of study of cultural and morphological properties of the isolated strains of microorganisms.

---

**Table 1. Results of isolation of microorganisms from national Kazakh sour milk drinks**

<table>
<thead>
<tr>
<th>№</th>
<th>Name of the microorganism</th>
<th>Source of isolation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>Lactobacillus delbrueckii subsp. bulgaricus</em></td>
<td>Koumiss, ayran</td>
</tr>
<tr>
<td>2</td>
<td><em>Lactobacillus acidophilus</em></td>
<td>Koumiss</td>
</tr>
<tr>
<td>3</td>
<td><em>Streptococcus thermophilus</em></td>
<td>Koumiss, ayran</td>
</tr>
<tr>
<td>4</td>
<td><em>Lactococcus lactis subsp. lactis</em></td>
<td>Ayran</td>
</tr>
<tr>
<td>5</td>
<td><em>Lactococcus lactis subsp. Lactis biovar diacetilactis</em></td>
<td>Ayran</td>
</tr>
<tr>
<td>6</td>
<td><em>Lactobacillus paracasei</em></td>
<td>Chegen</td>
</tr>
<tr>
<td>7</td>
<td><em>Lactobacillus fermentum</em></td>
<td>Chegen</td>
</tr>
<tr>
<td>8</td>
<td><em>Pediococcus damnosus</em></td>
<td>Chegen</td>
</tr>
<tr>
<td>9</td>
<td><em>Pediococcus acidilactici</em></td>
<td>Chegen</td>
</tr>
<tr>
<td>10</td>
<td><em>Lactobacillus gallinarum</em></td>
<td>Kurunga</td>
</tr>
</tbody>
</table>
Table 2. Characteristic of the cultural and morphological properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lactobacillus delbrueckii subsp. bulgaricus</th>
<th>Lactobacillus acidophilus</th>
<th>Streptococcus thermophilus</th>
<th>Lactococcus lactis subsp. lactis</th>
<th>Lactococcus lactis subsp. diacetylactis</th>
<th>Lactobacillus paracasei</th>
<th>Lactobacillus fermentum</th>
<th>Pediococcus damnosus</th>
<th>Pediococcus acidilactici</th>
<th>Lactococcus gallinarum</th>
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</thead>
<tbody>
<tr>
<td>Spore formation</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
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<td>Vagility</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>Size of bacteria (microns)</td>
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<td>0.9 x 5.3</td>
<td>0.7 x 1.0</td>
<td>0.7 x 4.3</td>
<td>0.6 x 1.0</td>
<td>0.9 x 2.6</td>
<td>0.9 x 1.0</td>
<td>0.8 x 1.0</td>
<td>0.6 x 1.0</td>
<td>6.0 x 0.7</td>
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<td>Edge pattern</td>
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<td>fringed</td>
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<td>wave-shaped</td>
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<td>convex</td>
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</tr>
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<td>skin-colored</td>
<td>skin-colored</td>
<td>skin-colored</td>
<td>skin-colored</td>
<td>skin-colored</td>
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<td>homogeneous</td>
<td>homogeneous</td>
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<td>homogeneous</td>
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<td>homogeneous</td>
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</tr>
<tr>
<td>Consistence</td>
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<td>soft</td>
<td>soft</td>
<td>soft</td>
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<td>soft</td>
<td>soft</td>
<td>soft</td>
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<td>soft</td>
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<td>Transparence</td>
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<td>non-transparent</td>
<td>mat</td>
<td>mat</td>
<td>non-transparent</td>
<td>non-transparent</td>
<td>mat</td>
</tr>
<tr>
<td>Gram-color staining</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
The results of studies of cultural and morphological properties of the microorganisms isolated from national Kazakh sour-milk drinks testify that the strains Lactobacillus delbrueckii subsp. bulgaricus, Lactobacillus acidophilus, Lactococcus lactis subsp. lactis biovar diacetilactis, Lactobacillus paracasei, Lactobacillus fermentum and Lactobacillus gallinarum have a stick-like shape from 0.6 x 3.5 to 6.0 x 0.7 microns in size characteristic of bacteria of the sort Lactobacillus. The microorganisms are Gram-positive, nonspore-forming, vagility is only observed in the strains Lactococcus lactis subsp. lactis biovar diacetilactis, Pediococcus damnosus and Pediococcus acidilactici.

Bacteria have a homogeneous structure soft in consistence. The consistence of colonies is only dense in Lactobacillus delbrueckii subsp. bulgaricus, Lactobacillus paracasei and Lactobacillus fermentum. The colonies of the studied microorganisms Lactobacillus delbrueckii subsp. bulgaricus, Lactobacillus acidophilus, Lactococcus lactis subsp. lactis, Lactobacillus paracasei, Lactobacillus fermentum and Lactobacillus gallinarum are mat, and the colonies of the strains Streptococcus thermophilus, Lactococcus lactis subsp. lactis biovar diacetilactis, Pediococcus damnosus and Pediococcus acidilactici are non-transparent.

The profile of colonies is various, too, thus, a flat profile of colonies was observed during the study in Lactobacillus delbrueckii subsp. bulgaricus, Lactobacillus acidophilus and Lactobacillus paracasei, and a convex profile of colonies in Streptococcus thermophilus, Lactococcus lactis subsp. lactis, Lactococcus lactis subsp. lactis biovar diacetilactis, Lactobacillus fermentum, Pediococcus damnosus and Pediococcus acidilactici. At the same time the edge pattern in Lactobacillus delbrueckii subsp. bulgaricus and Lactococcus lactis subsp. lactis is fringed, and it is straight in Streptococcus thermophilus. Lactobacillus gallinarum is characterized by an indistinct edge of the colony while the edge pattern of the colony in Lactobacillus acidophilus, Lactobacillus paracasei and Lactobacillus fermentum is wave-shaped.

The smooth surface of the colony is observed in five strains of microorganisms (Lactobacillus delbrueckii subsp. bulgaricus, Streptococcus thermophilus, Lactococcus lactis subsp. lactis and Lactobacillus paracasei and Lactobacillus gallinarum), and it is rough in the others. According to the results of the study, the color of the studied microorganisms varies from white to skin and grayish. The color of the colony in Lactobacillus gallinarum is grayish, and the skin color is observed in the strains Lactococcus lactis subsp. lactis and Lactobacillus fermentum. Colonies of white color are formed by the microorganisms of Lactobacillus acidophilus and Streptococcus thermophilus.

For the purpose of deeper identification of bacteria a microscopic examination was performed using the inverted microscope AxioVert.A1 (Carl Zeiss, Germany). In the course of microscopic examination the size of particles, the area and number of colonies were determined, besides, photographing of the studied samples the results of which are presented in Fig. 1 was performed.

Then, the physiological and biochemical properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks were studied. The identification of microorganisms only by cultural and morphological features is difficult due to the simplicity of geometry of microorganisms and the same structure of eukaryotic cell [17]. Besides, the physiological and biochemical properties allow to judge about the fitness of microorganisms to various external and internal factors of the environment and to increase the biomass of cultural cells to the maximum.

---

**Fig. 1.** Micrographs of native dabs of the strains of microorganisms isolated from the national Kazakh sour-milk drinks: (a) Lactobacillus delbrueckii subsp. bulgaricus; (b) Lactobacillus acidophilus; (c) Streptococcus thermophilus; (d) Lactococcus lactis subsp. lactis biovar diacetilactis; (e) Pediococcus damnosus; (f) Lactobacillus fermentum; (g) Lactobacillus gallinarum; (h) Lactococcus lactis subsp. lactis; (i) Lactobacillus paracasei; (j) Pediococcus acidilactici.
It is known that microorganisms differ from each other in biochemical properties – the ability to metabolize nutrients, antibiotic substances, various oxygen-containing organic compounds, such as carbohydrates, sugar, alcohols and organic acids, to synthesize enzymes, proteins, amino acids and vitamins [18].

The study of physiological and biochemical properties of bacteria allows to divide them by means of special culture media, to reveal their pertaining to a species and to divide them by strain. It is relevant for pure cultures, lactic and other kinds of bacteria used in the food industry [19].

Using the culture conditions and the composition of the medium, it is possible to determine the distinctive features of a microorganism used in taxonomy, the ecological niche and to find out a possibility of its use to solve practical tasks [17]. At last, the control of growth of cultures is the basis of biotechnological processes. All this emphasizes the importance of study of nature of growth and nutritious requirements of bacterial cultures. Table 3 provides the results of study of the physiological and biochemical properties of the strains isolated from national Kazakh sour-milk drinks.

The methods of study of physiological and biochemical strains of the microorganisms isolated from national Kazakh sour-milk drinks come down to the use of the microtests or the indicator paper systems which are a set of plastic holes with indicators. Some microorganisms can be identified by the ability to form stained compounds [20, 21].

The analysis of data of Table 3 allows to draw a conclusion that all the studied strains ferment ribose, D-galactose, D-glucose, D-fructose, D-mannose, N-acetyl-glucosamin, amygdalin, aesculin, salicin, cellobiose, maltose, lactose and D-sucrose which is characteristic of the representatives of the sort Lactobacillus. Strains considerably differ from each other in the consumption of other carbohydrates.

The research of antibiotic resistance of the strains of microorganisms isolated from national Kazakh sour-milk drinks is an important component in the course of complex study of microorganisms. A lot of microorganisms show resistance to the effect of antibiotics for several reasons. First, the resistance to the effect of antibiotic emerges with a change of genome as a result of multiple or single mutations. The acquired resistance descends further from one microorganism to another. As a result, a new population of microorganisms resistant to the effect of antibiotics emerges. Thus, there is a selection of bacterial cells. Secondly, microorganisms are capable to adapt in adverse conditions, in particular to the effect of antibiotic substances. As a result, the replacement of the metabolitic links of a microorganism, the natural course of which is broken by an antibiotic, with other metabolitic reactions resistant to the effect of the medicine occurs. Thirdly, microorganisms are capable to provide the synthesis of the substances destroying an antibiotic molecule in adverse conditions [22, 23].

Table 4 provides the results of the studies of antibiotic resistance of the strains of microorganisms isolated from national Kazakh sour-milk drinks.

The analysis of the empirical data provided in Table 4 testifies that bacterial cells are sensitive to the effect of the antibiotics that inhibit protein synthesis: laevomycin, tetracycline and doxycycline (the diameter of the zone of inhibition is at the level from 18.4 to 34.0 mm) and are to a lower degree sensitive to the effect of the aminoglycoside antibiotic substances that impede both protein synthesis and the processes of replication of a cell genome. Neomycin, sizomicin, kanamycin and streptomycin belong to such antibiotics (the width of zone of inhibition is at the level from 0 to 10.5 mm) [24].

These data confirm the belonging of the considered microorganisms to the group of Gram-positive bacteria. Besides, the results presented in Table 4 testify that all the studied strains are sensitive to the effect of β-lactam antibiotics which inhibit the synthesis of a cellular wall (ampicillin), except Streptococcus thermophilus.

The study of antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks is an important component of scientific research of the process of development of technology of a direct application starter as the antagonistic properties of microorganisms are the mechanism of functioning of microbiocenoses. In case of antagonism, some microorganisms oppress the development of other species, and sometimes they completely destroy it. The antagonistic properties are very widespread among microorganisms. Various populations of microorganisms have developed these or those methods of fight against their competitors. The antagonistic properties may consist in very fast reproduction, at the same time the microorganisms that grow fast push out and slow down the other microorganisms. And they can also relate to the synthesis of specific and nonspecific metabolites which can be formed not only during the cultivation of monocultures, but also in the presence of heterogeneous cultures. At the same time, co-culture provides the amplification of antagonistic properties of bacteria [25]. A method of co-culture on dense culture media was used to define the antagonistic activity of the strains of microorganisms isolated from national Kazakh sour-milk drinks. In the course of work, antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks using a diffusive method on a solid culture medium with the use of the following test strains were studied: Escherichia coli B-6954, Bacillus fastidiosus B-5651, Pseudomonas fluorescens B-3502, Pseudomonas aeruginosa ATCC 9027, Leuconostoc mesenteroides B-8404, Candida albicans ATCC 885-653 and Staphylococcus aureus ATCC 25923. Table 5 provides the results of the studies of antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks.
### Table 3. Distinctive physiological and biochemical features of the strains isolated from sour-milk Kazakh products

<table>
<thead>
<tr>
<th>Name of the substratum</th>
<th>Lactobacillus delbrueckii subsp. bulgaricus</th>
<th>Lactobacillus paracasei</th>
<th>Lactobacillus acidophilus</th>
<th>Lactobacillus fermentum</th>
<th>Lactococcus lactis subsp. lactis</th>
<th>Lactococcus lactis biovar diacetylactis</th>
<th>Pediococcus damnosus</th>
<th>Streptococcus thermophilus</th>
<th>Pediococcus acidilactici</th>
<th>Lactobacillus gasseri</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glycerin</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Erythritol</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>D-arabinose</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
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<td>-</td>
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**Designations:** “+” is a positive result; “-” is a negative result.
Table 4. Antibiotic resistance of the strains isolated from sour-milk Kazakh products

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<tr>
<th>Antibiotic</th>
<th>Lactobacillus delbrueckii subsp. bulgaricus</th>
<th>Lactobacillus paracasei</th>
<th>Lactobacillus acidophilus</th>
<th>Lactococcus lactis subsp. lactis</th>
<th>Lactococcus lactis subsp. diacetylactis</th>
<th>Pediococcus damnosus</th>
<th>Streptococcus thermophilus</th>
<th>Lactobacillus aciducitilis</th>
<th>Lactobacillus gasseri</th>
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</thead>
<tbody>
<tr>
<td>Ampicillin</td>
<td>32.0 ± 1.9</td>
<td>22.3 ± 1.3</td>
<td>30.5 ± 2.0</td>
<td>16.2 ± 1.2</td>
<td>21.6 ± 1.3</td>
<td>9 ± 0.1</td>
<td>17.6 ± 1.0</td>
<td>31.9 ± 1.9</td>
<td>35.7 ± 2.1</td>
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<td>Benzylpenicillin</td>
<td>20.7 ± 1.2</td>
<td>22.0 ± 1.3</td>
<td>19.0 ± 1.1</td>
<td>21.3 ± 1.3</td>
<td>19.3 ± 1.2</td>
<td>16.0 ± 1.1</td>
<td>18.5 ± 1.0</td>
<td>21.9 ± 1.2</td>
<td>24.8 ± 2.0</td>
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<tr>
<td>Doxycycline</td>
<td>18.4 ± 1.2</td>
<td>22.3 ± 1.3</td>
<td>31.5 ± 1.9</td>
<td>14.5 ± 1.2</td>
<td>12.6 ± 1.0</td>
<td>0 ± 0.1</td>
<td>17.6 ± 1.0</td>
<td>31.9 ± 1.9</td>
<td>35.7 ± 2.1</td>
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<td>26.8 ± 1.6</td>
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<td>Carbenicillin</td>
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<td>28.9 ± 1.7</td>
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<td>24.0 ± 1.6</td>
<td>26.0 ± 1.5</td>
<td>19.3 ± 1.2</td>
<td>28.4 ± 1.7</td>
<td>31.6 ± 1.8</td>
<td>14.8 ± 1.4</td>
<td>28.9 ± 1.7</td>
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<td>Methicillin</td>
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<td>21.0 ± 1.2</td>
<td>28.9 ± 1.7</td>
<td>12.6 ± 1.0</td>
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<td>14.9 ± 0.1</td>
<td>28.9 ± 1.7</td>
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<td>Tetracycline</td>
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<td>Cefalexin</td>
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<td>25.0 ± 1.5</td>
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Table 5. Antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks

<table>
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<tr>
<th>Name of the strain</th>
<th>Lactobacillus delbrueckii subsp. bulgaricus</th>
<th>Lactobacillus paracasei</th>
<th>Lactobacillus acidophilus</th>
<th>Lactococcus lactis subsp. lactis</th>
<th>Lactococcus lactis subsp. diacetylactis</th>
<th>Pediococcus damnosus</th>
<th>Streptococcus thermophilus</th>
<th>Lactobacillus aciducitilis</th>
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The analysis of empirical data on the study of antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks presented in Table 5 testifies that such natural strains as Escherichia coli B-6954, Bacillus fastidiosus B-5651, Pseudomonas fluorescens B-3502, Pseudomonas aeruginosa ATCC 9027, Leuconostoc mesenteroides B-8404, Candida albicans ATCC 885-653 and Staphylococcus aureus ATCC 25923 turned out to be the most sensitive to metabolites of lactic bacteria. Such strains as Lactobacillus delbrueckii subsp. bulgaricus, Lactococcus lactis subsp. lactis, Pediococcus acidilactici, Lactobacillus paracasei, Pediococcus damnosus and Lactobacillus gallinarum show the highest antagonistic activity. Thus, for example, the microorganism strain Lactobacillus delbrueckii subsp. bulgaricus has an adverse effect on the strains Bacillus fastidiosus B-5651 and Pseudomonas aeruginosa ATCC 9027; the strain Lactococcus lactis subsp. lactis has an adverse effect on the strains Bacillus fastidiosus B-5651, Pseudomonas fluorescens B-3502, Leuconostoc mesenteroides B-8404, Candida albicans ATCC 885-653 and Staphylococcus aureus ATCC 25923; the strain Lactobacillus paracasei shows antagonistic effect. Table 6 provides the results of the study.

Interpreting the results of the study presented in Table 6, we draw a conclusion that full compatibility is only characteristic of four strains – Lactobacillus gallinarum (kurring), Streptococcus thermophilus (koumiss), Lactococcus lactis subsp. lactis (ayran) and Pediococcus damnosus (chegen).

Thus, it was established during the study that of ten strains of microorganisms isolated from national Kazakh sour-milk drinks the most suitable for further studying for the purpose of development of technology of a direct application starter are the microorganisms isolated from kurunga – Lactobacillus gallinarum, koumiss – Streptococcus thermophilus, ayran – Lactococcus lactis subsp. lactis and chegen – Pediococcus damnosus.

Table 7 provides the compositions of culture media.

<table>
<thead>
<tr>
<th>Name of the strain</th>
<th>Lactobacillus delbrueckii subsp. bulgaricus</th>
<th>Lactococcus lactis subsp. lactis</th>
<th>Lactobacillus paracasei</th>
<th>Pediococcus acidilactici</th>
<th>Lactobacillus acidophilus</th>
<th>Lactobacillus fermentum</th>
<th>Lactococcus lactis subsp. lactis biovar</th>
<th>Pediococcus damnosus</th>
<th>Streptococcus thermophilus</th>
<th>Lactobacillus gallinarum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactobacillus delbrueckii subsp. bulgaricus</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>±</td>
<td>–</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Lactococcus lactis subsp. lactis</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>±</td>
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<td>–</td>
<td>+</td>
<td>±</td>
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<tr>
<td>Lactobacillus paracasei</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>±</td>
<td>±</td>
<td>–</td>
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<td>+</td>
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</tr>
<tr>
<td>Pediococcus acidilactici</td>
<td>±</td>
<td>+</td>
<td>–</td>
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<tr>
<td>Lactobacillus acidophilus</td>
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<td>±</td>
<td>+</td>
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<td>+</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Lactobacillus fermentum</td>
<td>±</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Lactococcus lactis subsp. lactis biovar</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>±</td>
<td>–</td>
<td>±</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Pediococcus damnosus</td>
<td>–</td>
<td>+</td>
<td>–</td>
<td>±</td>
<td>–</td>
<td>±</td>
<td>–</td>
<td>+</td>
<td>±</td>
<td>+</td>
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<tr>
<td>Streptococcus thermophilus</td>
<td>–</td>
<td>+</td>
<td>–</td>
<td>±</td>
<td>–</td>
<td>±</td>
<td>–</td>
<td>+</td>
<td>±</td>
<td>+</td>
</tr>
<tr>
<td>Lactobacillus gallinarum</td>
<td>–</td>
<td>+</td>
<td>±</td>
<td>–</td>
<td>±</td>
<td>±</td>
<td>–</td>
<td>±</td>
<td>+</td>
<td>±</td>
</tr>
</tbody>
</table>

Notes. “+” stands for biocompatible strains; “–” stands for incompatible strains; “±” stands for partially compatible strains.
Table 7. Variants of culture media for the cultivation of consortium of microorganisms

<table>
<thead>
<tr>
<th>Name of the component</th>
<th>Number of the culture medium depending on the content of components, g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>proteose-peptone</td>
<td>10</td>
</tr>
<tr>
<td>meat extract</td>
<td>15</td>
</tr>
<tr>
<td>yeast extract</td>
<td>10</td>
</tr>
<tr>
<td>glucose</td>
<td>15</td>
</tr>
<tr>
<td>Tween-80</td>
<td>1</td>
</tr>
<tr>
<td>ammonium citrate</td>
<td>2</td>
</tr>
<tr>
<td>sodium acetate</td>
<td>5</td>
</tr>
<tr>
<td>magnesium sulfate</td>
<td>0.1</td>
</tr>
<tr>
<td>manganic sulfate</td>
<td>0.05</td>
</tr>
<tr>
<td>sodium hydrophosphate</td>
<td>0.5</td>
</tr>
<tr>
<td>agar-agar</td>
<td>12.0</td>
</tr>
<tr>
<td>methyl rosaniline</td>
<td>0.0001</td>
</tr>
<tr>
<td>casein hydrolysate</td>
<td>15.0</td>
</tr>
<tr>
<td>papain digest of soy flour</td>
<td>5.0</td>
</tr>
<tr>
<td>sodium chloride</td>
<td>4.0</td>
</tr>
<tr>
<td>sodium citrate</td>
<td>0.5</td>
</tr>
<tr>
<td>sodium sulphite</td>
<td>0.1</td>
</tr>
<tr>
<td>L-cystine</td>
<td>0.1</td>
</tr>
<tr>
<td>potassium phosphate dibasic</td>
<td>1.5</td>
</tr>
<tr>
<td>sodium azide</td>
<td>0.05</td>
</tr>
<tr>
<td>ammonium citrate dibasic</td>
<td>1.2</td>
</tr>
<tr>
<td>sodium acetate</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The analysis of results of the choice of optimum composition of culture medium for the cultivation of symbiotic consortium of the microorganisms provided in Fig. 1 testifies that the maximum viability and activity of the microorganisms which are part of consortium is observed when it is cultivated on culture medium No. 2. The concentration of microorganisms amounts to 28.3 CFU/g after 24 h of cultivation on culture medium No. 2 $10^6$ which is 15% higher than the concentration of the microorganisms grown up on culture medium No. 3 and is 32% higher than the concentration of the microorganisms grown up on culture medium No. 4 under equal conditions.

Fig. 2 provides the results of selection of composition of culture medium for the cultivation of consortium of microorganisms.

![Fig. 2. Influence of composition of culture medium on the viability and activity of symbiotic consortium: (1) culture medium No. 1; (2) culture medium No. 2; (3) culture medium No. 3; (4) culture medium No. 4.](image-url)
CONCLUSIONS

(1) Such strains of lactobacilli as Lactobacillus delbrueckii subsp. bulgaricus, Lactobacillus acidophilus, Streptococcus thermophilus, Lactococcus lactis subsp. lactis, Lactococcus lactis subsp. lactis biotype diacetylactis, Lactobacillus paracasei, Lactobacillus fermentum, Pediococcus damnosus, Pediococcus acidilactici and Lactobacillus gallinarum have been isolated from national sour-milk food products: chegen, ayran, koumiss, kurunga. It has been shown that strains considerably differ from each other in the consumption of other carbohydrates. It has been established that the studied strains are sensitive to the effect of β-lactam antibiotics which inhibit the synthesis of cellular wall (ampicillin), except Streptococcus thermophilus. The analysis of biocompatibility has shown that full compatibility is only characteristic of four strains – Lactobacillus gallinarum (koumis), Streptococcus thermophilus (koumiss), Lactococcus lactis subsp. lactis (ayran) and Pediococcus damnosus (chegen).

(2) Cultural, morphological, physiological and biochemical properties have been studied, antibiotic resistance, antagonistic activity and biocompatibility of the microorganisms isolated from national Kazakh drinks have been determined. It has been established that the isolated microorganisms have a stick-like shape of 0.6 x 3.5 to 6.0 x 0.7 microns in size characteristic of bacteria of the sort Lactobacillus and are Gram-positive and nonspore-forming. It has been shown that strains considerably differ from each other in the consumption of other carbohydrates. It has been established that all the studied strains are sensitive to the effect of β-lactam antibiotics which inhibit the synthesis of cellular wall (ampicillin), except Streptococcus thermophilus.

REFERENCES


GRAPE POMACE EXTRACT AND PEAR IN SNACK PRODUCTION TECHNOLOGY

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Abstract: The article is devoted to the study of the influence of process parameters for the production of pear snacks with the addition of grape extract secondary raw materials on the chemical composition and antioxidant activity of the resulting product. This paper describes the selection of the most optimum conditions for production of high quality, competitive product with the highest antioxidants activity. The object of the study were temperature, time of soaking pear slices in the extract, drying process. Analysis on the content of total amount of phenolic compounds the content of Gallic acid, flavonoids and tannins content of catechin, anthocyanin content cyanidin-3-glycoside, antiradical capacity using the free radical DPPH method (2,2-diphenyl-1-picrylhydrazy), antioxidant activity by the method of ABTS (2,2’-settlement Azino-bis(3-ethylbenzthiazoline-6-sulfonic acid), which restores the force by the method of FRAP (ferric reducing antioxidant power), antioxidant activity in linoleic acid system. The obtained results are vivid enough and allow us to conclude that the best way to obtain high-quality resulting product out of pear fruit crop is freeze-drying, and the shelf life of an opened package in no longer than 38 hours. This study was financially supported by the Ministry of Education and Science of the Russian Federation within the basic part of the government task number 2014/199 FSBEI HPE Samara State Technical University by the project «Creating Scientific Methodology of Developing Formulation and Technologies of Food Products Fighting Oxidant Stress in Human’s Body» code 974.

Keywords: Pears, snack, antioxidant activity, extract, grape, freeze drying

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INTRODUCTION

Pear is one of the major crops and is highly valued for its taste and technological qualities of the fruit. [1] Pear fruits are characterized by medical and nutritional value. They contain sugar, acids, tannins, mineral nutrients, vitamins, pectin substances. Especially pear fruits are valuable for containing such an important substance for the human organism as chlorogenic acid, and arbutin. There is more chlorogenic acid in pear fruit than in apples, and its amount depending on the class is of 30–70 mg%. It has healing properties for liver diseases [2].

Shelf life of pears is small, so raw fruit processing is becoming an important area of food industry. One of the main stages which determines the quality of the manufactured product is the selection of technological modes. The mode is called optimal when the product is produced with the best rates and efficiency of the process is the highest.

The aim of this work is the development of pear snack production technology with addition of an extract [3] of the secondary raw grape materials. In addition, we studied the effect of technological parameters on physical and chemical [4] and antioxidant rates [5] of the finished product. To develop the technology of obtaining a functional food item - pear snacks – some research was conducted on the effect of pear slices thickness, a mass fraction of extract for soaking pear slices, temperature of soaking pear slices in the extract, drying technology, technological modes of drying on the organoleptic, physical and chemical, structural and mechanical rates of finished products.

OBJECTS AND METHODS OF STUDY

Chemicals and reagents. Folin-Ciocalteu reagent in sodium carbonate, gallic acid, catechin, ABTS (2,2’-azino-bis (3-ethylbenzthiazoline-6-sulfonic acid) were purchased from Fluka (Germany). DPPH (2,2-diphenyl-1-picrylhydrazy), Tween 40, hydrogen peroxide, sodium nitrite, aluminum chloride, thiobarbituric acid, trichloroacetic acid were purchased from Sigma-Aldrich Chem. mp. (USA).

Fruit collection. The grapes and pears collected on the territory of the Russian Federation at the enterprise wineries in the city of Samara in 2014.

Determination of total phenols. Total phenolic content of methanolic fruit extracts was assessed using a modified version of the Folin–Ciocalteu assay [6]. Gallic acid was used as a standard and the aqueous gallic acid solution (200 mg l 1) was diluted with distilled water to give appropriate concentrations for a
standard curve. For the analysis, 100 ll of methanolic fruit extract or gallic acid standard, 100 ll of methanol, 100 ll of Folin–Ciocalteu reagent and 700 ll of Na₂CO₃ were added into 1.5 ml micro-centrifuge tube. The samples were vortexed immediately and the tubes were incubated in the dark for 20 min at room temperature. After incubation all samples were centrifuged at 13,000 rpm for 3 min. The absorbance of the supernatant was then measured at 735 nm in 1 ml plastic cuvettes using evolution 200 Series spectrophotometer. The results were expressed in mg gallic acid equivalent/100 g dry weight.

**Determination of total flavonoids.** The flavonoid content of the methanolic extracts was measured using a assay [7]. A known volume (0.5 ml) of the extract or standard solution of quercetin was added to a 10 ml volumetric flask. Distilled water was added to make a volume of 5 ml. At zero time, 0.3 ml of 5% w/v NaNO₂ was added to the flask. After 5 min, 0.6 ml of 10% w/v AlCl₃ was added and after 6 min, 2 ml of 1 M NaOH was added to the mixture followed by the addition of 2.1 ml distilled water. Absorbance was read at 350 nm against the blank (water) and flavonoid content was expressed as mg quercetin equivalents in 100 g of fresh material.

**Determination of the anthocyanin profile.** The concept of determining the amount of anthocyanin present in a material by measuring the change in absorbance at 2 different pH values (3.4 and 2.0) [8]. Researchers have proposed using the pH values of 1.0 and 4.5 (2–5). Monomeric anthocyanins undergo a reversible structural transformation as a function of pH (colored oxonium form at pH 1.0 and colorless hemiketal form at pH 4.5). Thus, the difference in absorbance at the vismax (520 nm) of the pigment is proportional to the concentration of pigment. Degraded anthocyanins in the polymeric form are resistant to color change with change in pH. Therefore, polymerized anthocyanin pigments are not measured by this method because they absorb both at pH 4.5 and 1.0.

**Determination of condensed tannins.** In presence of concentrated H₂SO₄, condensed tannins were transformed by the reaction with vanillin to anthocyanidols [9]. 50 l of the methanolic seed extract appropriately dilute was mixed with 3 ml of 4% methanol vanillin solution and 1.5 ml of H₂SO₄. After 15 min, the absorbance was measured at 500 nm. Condensed tannin contents of seeds (three replicates per treatment) were expressed as mg catechin equivalents (CE) per gram of dry weight through the calibration curve with catechin. The calibration curve range was 50–600 mg ml⁻¹.

**DPPH radical scavenging activity.** The scavenging activity of samples was measured in accordance with the method [10]. The method was based on the reduction of methanolic DPPH in the presence of a hydrogen-donating antioxidant. DPPH solution was an intense violet colour and showed an absorption band at 515 nm. Adsorption and colour lowered when DPPH was reduced by an antioxidant compound. The remaining DPPH corresponded inversely to the radical-scavenging activity of the antioxidant. DPPH (2 mg) was dissolved in 54 ml of MeOH. Aliquots of investigated extract (50, 100, 200, 300, 500 and 1000 lg) were dissolved in 2 ml of MeOH. Then 1.0 ml of each solution was added to 2.0 ml of DPPH solution at room temperature. The absorbance at 515 nm was measured against a blank (2 ml MeOH in 2.0 ml of DPPH solution) using evolution 200 Series spectrophotometer. The results were expressed as percent-age of reduction of the initial DPPH adsorption by test samples:

\[
\text{% of reduction of the initial DPPH adsorption} = \frac{ADPPH(t)_{Asample} - ADPPH(t)_{Sample}}{ADPPH(t)_{Sample}} \times 100
\]

**FRAP assay.** The FRAP assay was carried [11]. The FRAP solution was freshly prepared on the day of use, by mixing acetate buffer (pH 3.6), ferric chloride solution (20 mM) and TPTZ solution (10 mM TPTZ in 40 mM HCl) in a proportion of 10 : 1 : 1, respectively. Following this the FRAP solution was heated, while protected from light, until it had reached a temperature of 37 LC. Appropriate dilutions of methanolic fruit extracts were prepared. One hundred microlitres of the diluted sample extract (or for blank 100 ll methanol and for Trolox standard curves 100 ll Trolox of appropriate concentration) and 900 ll of FRAP solution were added into a micro-centrifuge tubes. The tubes were vortexed and left at 37 LC for exactly 40 min, and the absorbance was measured at 593 nm. The Trolox standard curves were used to calculate the antioxidant activity of the samples in relation to Trolox and were expressed as mg Trolox equivalent/100 g dry weight sample (mg TE 100 g 1 DW).

**ABTS free radical decolorization assay.** The total antioxidant capacity assay conducted using evolution 200 Series spectrophotometer. The procedure was based on a method [12] with some modification. ABTS + was generated by reacting ABTS (7.4 mM) with potassium persulphate (2.6 mM). The solution was diluted to obtain an absorbance of 1.4 units at 414 nm (molar extinction coefficient E = 3.6_10⁴ mol_1 1 cm_1). Forni, Morla-Arellano, Packer, & Willison (1986) with 50 mM glycine-HCl buffer (pH 4.5) before use. Three millilitres of the solution were added to 20–80 ml of AA, trolox, hydroquinone, pyrogallol and fruit extracts separately. The changes in absorbance at 414 nm were recorded at 1, 3, 6, 10, 20, 30, 40, 60 and 90 min after mixing and until the absorbance reached a plateau. The antioxidant capacities, obtained by comparing the absorbance change at 414 nm in a test reaction mixture containing extract of fruit with that containing AA, were expressed as mg of AA equivalents per 100 g of homogenate (AEAC).

**Determination of Antioxidant Activity in a Linoleic Acid System.** The total antioxidant activity of FEHP was carried out by use of a linoleic acid system [13]. The linoleic acid emulsion was prepared by mixing 0.2804 g of linoleic acid, 0.2804 g of Tween 20 as emulsifier, and 50 ml of phosphate buffer (0.2 M, pH 7.0), and then the mixture was homogenized. A 0.5 ml ethanol solution of different
Concentration of FEHP (50–500 μg/mL) was mixed with linoleic acid emulsion (2.5 mL, 0.2 M, pH 7.0) and phosphate buffer (2 mL, 0.2 M, pH 7.0). The reaction mixture was incubated at 37°C in the dark to accelerate the peroxidation process. The levels of peroxidation were determined according to the thiocyanate method by sequentially adding ethanol (5 mL, 75%), ammonium thiocyanate (0.1 mL, 30%), sample solution (0.1 mL), and ferrous chloride (0.1 mL, 20 mM in 3.5% HCl). After the mixture was left for 3 min, the peroxide value was determined by reading the absorbance at 500 nm on a spectrophotometer.

RESULTS AND DISCUSSION

Based on the example of soaking pear slices in grape extract the dependence of physical and chemical and antioxidant properties of snacks on mass fraction of the added extract was revealed. Four samples of the product with a mass fraction of the extract of 20, 40, 60 and 80% of the feedstock mass were prepared.

Comparative analysis has shown (Table 1) that with increasing concentrations of grapes pomace extract, chemical composition rates increase. Thus, comparing the concentration of 20 and 80% we can observe that there is a 4 times increase in flavonoid (110 and 437 mg of catechin/100 grams of feedstock, respectively), and the anthocyanins and tannins increase almost by 10 times.

Studying the rates in Fig. 1, we can also see an increase in the restoring force rates and the antioxidant capacity of pear snack with the addition of grapes pomace extract compared with the feedstock. Thus comparing the feedstock with pear snack soaked in 80% extract the restoring force rates and antioxidant capacity are increased by 6 times.

After analyzing the data of Fig. 2, in terms of antiradical activity rate EC50 (extract concentration required to bind 50% of free radicals DPPH) the feedstock does not show any anti-radical activity. The greatest antiradical activity was shown by pear slices soaked in 80% extract (EC50 = 94 mg / ml).

Thus, it can be concluded that soaking pear slices in the extract of different concentrations leads to an increase of the chemical composition and antioxidant properties as compared with the feedstock.

Table 1. The change of pear snack chemical composition with the addition of extract with different concentration

<table>
<thead>
<tr>
<th>Extract %</th>
<th>Total content of phenols, mg of gallic acid/100 g of material</th>
<th>Total content of flavonoids, mg of catechine/100 g of material</th>
<th>Total content of anthocyanins, mg of cyanidin-3-glycoside/100 g of material</th>
<th>Total content of tannins, mg of catechine/100 g of material</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>118</td>
<td>47</td>
<td>Absent</td>
<td>0.12</td>
</tr>
<tr>
<td>20</td>
<td>110</td>
<td>31</td>
<td>3.18</td>
<td>0.12</td>
</tr>
<tr>
<td>40</td>
<td>189</td>
<td>136</td>
<td>4.23</td>
<td>0.16</td>
</tr>
<tr>
<td>60</td>
<td>224</td>
<td>189</td>
<td>25.24</td>
<td>0.88</td>
</tr>
<tr>
<td>80</td>
<td>437</td>
<td>314</td>
<td>31.6</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Fig. 1. Study of restoring force and antioxidant activity.
The analysis of the data in the Table 2 allows to conclude that with the increasing temperature of pear samples soaked in 80% extract, chemical composition rates increase.

As seen in Fig. 3, the highest concentration of Ec50, and consequently, the lowest activity against trapping radicals found in pears soaked in extracts at 5°C. Pears soaked in room temperature extract and 35°C extract have lower values of the active concentration, hence higher antiradical activity. By the ability to capture radicals ABTS, all the temperatures of soaking pear slices in grape pomace extract are about the same level.

In the analysis of the Fig. 4 we can notice that pear samples soaked in the extract at 35°C have the greatest restoring force, the pear samples soaked in the extract at room temperature differ slightly. The ability of pears to inhibit the oxidation of linoleic acid in model system, is characterized as the antioxidant activity. The highest antioxidant activity is shown in pear samples soaked in room temperature extract. In case of heating the extract pears showed the least antioxidant activity compared to other monitored temperatures.

The room temperature of 20–22°C was chosen from all the monitored temperatures, because in terms of chemical composition and antioxidant properties it is slightly different from the temperature of 35°C. In addition, the use of room temperature will allow to reduce extra energy usage.

There is some specific interest in measuring the mass fraction of soluble solids in the processed pear slices, both before and after heat treatment (Fig. 5).

Table 2. The Change of chemical composition of pear snacks

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Total content of phenols, mg of gallic acid/100 g of material</th>
<th>Total content of flavonoids, mg of catechin/100 g of material</th>
<th>Total content of anthocyanins, mg of cyanidin-3-glycoside/100 g of material</th>
<th>Total content of tannins, mg of catechin/100 g of material</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°C</td>
<td>191</td>
<td>186</td>
<td>57.77</td>
<td>1.22</td>
</tr>
<tr>
<td>20°C</td>
<td>425</td>
<td>302</td>
<td>61.29</td>
<td>4.06</td>
</tr>
<tr>
<td>35°C</td>
<td>432</td>
<td>312</td>
<td>62.79</td>
<td>4.54</td>
</tr>
</tbody>
</table>

Fig. 2. Study of antioxidant activity.

Fig. 3. Study of antioxidant properties.
Fig. 4. Study of the restoring force and antioxidant activity.

Fig. 5. Mass fraction of soluble solids.

Fig. 5 shows the average data on the change of the mass fraction of soluble solids in fresh pears and pears soaked in the extract at different temperatures. Sliced pear fruits were kept in grapes pomace extract for one hour at 5°C, 25°C and 35°C. As a result of the work the direct dependence of the loss of soluble solids from the extract temperature was observed. During the data processing the loss of the mass fraction of soluble solids in the leaching and the removal of air contained in the intercellular tissue spaces of pear slices was revealed. On average, after treatment, the samples lost by 1 to 2% solids.

For obtaining the final product - pear snacks – three kinds of drying were researched: convective at 70°C, IR drying at 70°C, freeze-drying.

Table 3 shows that the highest content of phenolic compounds (458 mg of gallic acid / 100 g of feedstock) and flavonoids (317 mg of catechin / 100 g of feedstock) is had by pear snacks dried in freeze-drying. This type of drying preserves the greatest amount of anthocyanins (63.8 / 100 grams of feedstock) and tannins (2.52 mg of catechin / 100 grams of feedstock). It should also be noted that the heat treatment of pear snack is inferior to freeze drying on the total content of phenolic compounds, flavonoids, anthocyanins and tannins.

According to the Fig. 6 data it can be concluded that the highest antiradical activity, characterized by the lowest concentration of the extract (EC50) necessary for the binding of free radicals 50% 2,2-diphenyl-1-picrylhydrazyl (DPPH), is shown in freeze-dried pear snacks.

The highest antioxidant activity (15.1%) and the restoring force (15.1 mmol Fe2+ / 1 kg IP) belongs to pear snacks which are also freeze-dried (Fig. 7). Low antioxidant activity (10.2%) and the restoring force (7.38 mmol Fe2+ / 1 kg IP) are observed in snacks dried using IR method.

Practically all kinds of heat treatment decrease the antioxidant capacity of snacks. This is explained by the following: not only the phenolic substances, flavonoids, but also vitamins C, A, E, the enzyme system of the cell possess the antioxidant activity in plant cells as well. When heated these antioxidants are apparently destroyed and there is antioxidant activity inherent in the phenolic antioxidant complex left.
Table 3. Study of chemical composition of final product dried in different ways

<table>
<thead>
<tr>
<th>Drying type</th>
<th>Total content of phenols, mg of gallic acid/100 g of material</th>
<th>Total content of flavonoids, mg of catechine/100 g of material</th>
<th>Total content of anthocyanins, mg of cyanidin-3-glycoside/100 g of material</th>
<th>Total content of tannins, mg of catechine/100 g of material</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>211</td>
<td>251</td>
<td>Absent</td>
<td>2.40</td>
</tr>
<tr>
<td>Convective</td>
<td>314</td>
<td>285</td>
<td>24.57</td>
<td>1.54</td>
</tr>
<tr>
<td>Freeze</td>
<td>458</td>
<td>317</td>
<td>63.80</td>
<td>2.52</td>
</tr>
</tbody>
</table>

During the convective snack drying method initially drying process is sufficiently effective. However, as the product of dehydration and the consequent decrease in its heat- and mass-providing characteristics, an increasing share of thermal energy does not flow inside the dried products [14]. The energy output of the process is grows, drying time increases, there are local overheating of the product, which is reflected in the quality of the finished snack.

In terms of convective heating the product is heated up primarily due to heat-and-moisture providing which is determined by thermal diffusion of moisture. Because of the small thermal conductivity capacity at 70°C drying flows for long enough, even with a small sample thickness, moisture evaporation is slow, which is to be explained by increased content of strongly bound moisture as well.

Using a vacuum freeze drying allows to reduce the process duration in 2–3 times, to improve structural and rheological characteristics as well as to achieve a water activity rate that ensures microbiological stability of the product, organoleptic characteristics typical of dry products.
In this connection, the possibility of using freeze drying, resulting in the process which is the inverse of condensation has been studied. Thus the fluid is displaced by a completely different method, which contributes to a higher quality and, of course, useful products. First, the product undergoes a deep freeze, and then the moisture is “dried” out of it under the pressure.

The research resulted in development of the technology for snack production including the following operations: acceptance of raw materials, cleaning, inspection, seed chamber removal, cutting, soaking, freeze-drying, re-inspection, pre-packing, packing (Fig. 8).

These pear snacks dried with three different methods were analyzed on organoleptic and biochemical parameters. Fig. 9 shows comparative data of physical-chemical rates of fruit snacks prepared by freeze, convective and IR drying methods.

The content of moisture mass fraction in fruit snacks, prepared by convective drying method is 4.7 ± 0.1%, at snacks dried by IR-method it is 4.6 ± 0.1%, while for chips prepared by freeze method it is about 4.8 ± 0.1 %. The average content of titratable acids in fruit snacks, prepared by convective drying and IR methods is 2.3 ± 0.1%, for the snacks prepared by freeze method is 2.4 ± 0.1%. The content of reducing substances in the fruit snack prepared by convection, freeze and IR drying methods range from 27.3 to 27.9%.

So the pear snacks tasting with the addition of grape pomace extract obtained by convective, infrared, and freeze-drying, received the following tasting evaluation (Fig. 10).

Fig. 8. Flow chart.

Fig. 9. Comparative analysis of physical-chemical rates of fruit snacks prepared by convective, freeze and IR drying methods.

Fig. 10. Tasting evaluation of pear samples with the addition of grape pomace extract dried by different drying methods.
Analyzing the tasting evaluation data corresponding to the high quality of the final product, it must be concluded that the freeze drying method is the most advantageous one in the production of pear snacks with the addition of grape pomace extract, a freeze drying method.

Microbiological spoilage of food is determined by huge variety of bacteria, molds and yeasts. Safety of the studied pear snacks was evaluated by 3 factors (Table 4):

1. The number of mesophilic aerobic and facultative anaerobic microorganisms QMAFANM - a criterion which at 30°C for 48–72 hours allows to reveal all groups of microorganisms growing in certain environments. The identification of QMAFANM was carried out according to All Union State Standard 10444.15-94 (23).

2. The number of coliform bacteria (All Union State Standard 31747-2012) (34 ells).

3. Mold and yeast were determined according to All Union State Standard P 10444.12 (36 ells).

Tests were conducted in an accredited testing laboratory of Hygiene and Epidemiology Centre in the Samara region.

Based on the data available, it can be concluded that the microbiological rates of pear snacks with high antioxidant properties prepared by freeze-drying, fully meet the requirements of TR CU 021/2011 "On food safety".

The shelf life of food is one of the most important indicators, which depends on many factors: the quality of the raw material used, sanitary conditions of production, technology, equipment, storage and packaging conditions.

During the storage, studies of physical and chemical rates and antioxidant properties of natural pear snacks and snacks with grape pomace extract were carried out. Experimental snack samples were packaged in foil and paper bags, laminated with heat-sealable materials approved for use by the institutions of Russian Federal Service for Consumer Rights Protection and Human Welfare, and providing the quality of product safety during storage and transportation. Storaged packaged snacks were evaluated in terms of shelf life, physical, chemical, organoleptic rates and content of the antioxidant activity with a period of 3 months. Recommended storage time during freeze-drying method is 12 months with a relative humidity of 60% and a temperature of 23°C.

The results of physical and chemical rates are showed in Table 5.

Based on data in Table 5 we can conclude that by the study of physical and chemical parameters of snacks with higher antioxidant properties during 12 months’ storage, the content of moisture mass fraction, acidity and reducing substances vary within established norms.

Studies of the content of antioxidant activity in pear snacks with enhanced antioxidant properties showed that during the storage rates have not changed unlike those of natural snacks (Table 6).

Study of Table 6 allows to conclude, that the grape pomace extract has a prolonging effect on the antioxidant properties of the final product during the storage.

The freshly collected samples were also analyzed for the duration of storage on the content of moisture mass fraction in accordance with All Union State Standard 5900-73 "Food concentrates. Methods for determination of moisture " (24) with a time period of 3 hours.

Table 4. Microbiological rates of snacks with antioxidant hyperactivity

<table>
<thead>
<tr>
<th>Rates, measurement unit</th>
<th>Allowable levels</th>
<th>Actual Value</th>
<th>Normative Documents on Testing Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total microbial number, KOE/g</td>
<td>Not more than 1×103</td>
<td>Less than 1.0×101</td>
<td>All Union State Standard 10444.15-94</td>
</tr>
<tr>
<td>Coliform, g</td>
<td>Is not allowed in 1.0</td>
<td>Not found in 1.0</td>
<td>All Union State Standard 31747-2012</td>
</tr>
<tr>
<td>Mold, KOE/g</td>
<td>Not more than 50</td>
<td>Less than 10</td>
<td>All Union State Standard 10444.12</td>
</tr>
<tr>
<td>Yeast, KOE/g</td>
<td>Not more than 50</td>
<td>Less than 10</td>
<td>All Union State Standard 10444.12</td>
</tr>
</tbody>
</table>

Table 5. Physical and chemical rates of pear snacks during the storage

<table>
<thead>
<tr>
<th>Rates</th>
<th>Object</th>
<th>Fresh snacks</th>
<th>After 12 months’ storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture Mass fraction, %</td>
<td></td>
<td>4.8 ± 0.3</td>
<td>4.9 ± 0.3</td>
</tr>
<tr>
<td>Titratable acidity, % calculated as Apple acidity</td>
<td></td>
<td>2.4 ± 0.1</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>Content of soluble solids, %</td>
<td></td>
<td>27.9 ± 0.4</td>
<td>27.5 ± 0.4</td>
</tr>
</tbody>
</table>
Table 6. Study of chemical composition and antioxidant activity of pear snacks during the storage

<table>
<thead>
<tr>
<th>Products of long-term storage</th>
<th>Total content of phenols, mg of gallic acid/100 g of material</th>
<th>Total content of flavonoids, mg of catechine/100 g of material</th>
<th>$E_{50}$, mg/cm$^3$</th>
<th>FRAP value mmol Fe$^{2+}$/1 kg of raw material</th>
<th>Antioxidant activity, Inhibiting %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pear snacks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 months’ storage</td>
<td>116.3</td>
<td>46.3</td>
<td>169.3</td>
<td>1.73</td>
<td>4.6</td>
</tr>
<tr>
<td>6 months’ storage</td>
<td>112.7</td>
<td>43.4</td>
<td>174.8</td>
<td>1.67</td>
<td>4.1</td>
</tr>
<tr>
<td>9 months’ storage</td>
<td>109.3</td>
<td>40.1</td>
<td>190.4</td>
<td>1.23</td>
<td>4.1</td>
</tr>
<tr>
<td>12 months’ storage</td>
<td>87.6</td>
<td>39.7</td>
<td>198.7</td>
<td>1.14</td>
<td>3.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pear snacks with higher antioxidant properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 months’ storage</td>
</tr>
<tr>
<td>6 months’ storage</td>
</tr>
<tr>
<td>9 months’ storage</td>
</tr>
<tr>
<td>12 months’ storage</td>
</tr>
</tbody>
</table>

Fig. 11. Change of moisture mass fraction in final product without package.

It was found that in case of an opened package during the time crunch indicator decreases (Fig. 11), thus it is not recommended to store the opened package for more than 38 hours. The critical moisture content is 8%, as at higher humidity of the product development of microorganisms occurs.

The obtained results are quite illustrative and allow us to conclude that freeze-drying is the best way to produce a high quality final product of fruit crops of pears.

ACKNOWLEDGEMENTS

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72
OPTIMIZATION OF TECHNOLOGICAL PARAMETERS OF PREPARATION OF DOUGH FOR RUSKS OF HIGH NUTRITION VALUE

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Abstract: The work has been performed on the basis of Department of technology of baking, confectionery, macaroni and grain processing productions of Voronezh State University of Engineering Technologies. The urgent line of development of the baking industry is the development of new formulations and resource-saving technologies of dry bread products of high nutrition value and functional orientation. The application of flour made of wholemeal wheat instead of high-quality wheat flour is perspective to realize it. An important condition to obtain consistently high-quality products and increase production efficiency is the establishment of optimum technological parameters of preparation of dough. Mathematical methods of planning of experiment are applied to study the interaction of the major technological factors influencing the process of preparation and the quality of dry bread products. The following are chosen as the major factors: the dosage of flour made of wholemeal wheat and the humidity of dough. The main indicator of quality of rusks characterizing their swelling capacity in water – the swelling capacity coefficient – was the output parameter. The optimization of parameters of preparation of dough for rusks was performed using experimental and statistical methods. As a result of the performed experiment a mathematical model in the form of regression equation which adequately describes the studied process has been developed. The statistical processing of experimental data has been performed according to Student, Kolkiren and Fischer criteria (with the confidential probability of 0.95). The mathematical and graphic interpretation of regression equation have allowed to determine previously the optimum area of factorial space in which the highest value of output parameter is reached. The optimization of technological parameters of preparation of dough in the value of swelling capacity coefficient of rusks was performed using the method of Lagrange multipliers. Rational values of factors have been determined: the dosage of flour made of wholemeal wheat is 99.82%, the humidity of dough is 40.86%. Their choice has been validated by a series of parallel experiments which has shown sufficient convergence of results with the average square error of no more than 0.67%. On the basis of the obtained data a formulation and a way of production of rusks of high nutrition value "Cracking delicacy" has been developed.

Keywords: Flour made of wholemeal wheat, rusks, swelling capacity coefficient, central composite rotatable uniform planning, optimization


INTRODUCTION

The technologies of ecologically safe resource-saving production and processing of agricultural raw materials and food products play a fundamental role in the social and economic development of the state. The implementation of programs for the creation of waste-free and low-waste complex technologies is based on the modern scientific achievements and their practical realization. One of the effective measures is the introduction of innovative technology of processing of wheat grain into flour made of wholemeal wheat and its use in baking production. Such a technology will allow to increase the quality and nutrition value of production, to reduce its prime cost, to intensify the technological process, will provide an opportunity for the enterprise to react more flexibly to market conditions. Thanks to the application of disintegration-wave method of crushing, flour made of wholemeal wheat is characterized by a 100% output, high dispersion (on average, 38–40 microns) and a high nutrition value. It preserves all the components of grain having a high potential in the content of protein and irreplaceable amino acids, food fibers, vitamins and mineral substances. The expediency of application of flour made of wholemeal wheat in the production of bakery products of wide range, including that for dietetic and preventive nutrition has been established by the performed researches. The regular use of...
products made of this flour provides the activation of human's own microflora, the improvement of digestion processes and an increase in the accessibility of other products [1, 2].

One of the types of bakery products is rich rusks – the products with low humidity, a high nutritional value and a long period of storage allowing their use in remote regions of the country. Dry bread products are very popular with all the age groups of the population. According to Rosstat [the Federal State Statistics Service], the volume of their production in Russia steadily increases for the last 5 years, the annual gain averages 3–4%. In this regard, the development of new formulations and technologies of dry bread products of high nutrition value and functional orientation is urgent. At the same time, an important condition to obtain consistently high-quality products and increase production efficiency is the establishment of optimum technological parameters of preparation of dough. The purpose of work was the study of interaction of the major technological factors influencing the process of preparation and the quality of dry bread products, the search of their optimum values with the use of methods of mathematical modeling.

**STUDY OBJECTS AND METHODS**

The objects of the study were dry bread products. Children's rusks developed in accordance with GOST 8494-96 have been taken as a basis. The dough for test specimens was prepared in the accelerated way, at the same time they replaced high-grade wheat flour by flour made of wholemeal wheat, butter – by mustard, the mass of sugar was reduced by 1/3, the mass of yeast was increased by 0.6 kg, they also added whey in the amount of 15 kg per 100 kg of flour according to the formulation. The duration of dough fermentation was 90 min. to the acidity of 4.0–4.5 degrees. The fermented dough was subjected to cutting and proving for 50 min. and baking for 15 min. at a temperature of 210–220°C. The baked dry bread plates were held at a temperature of 18–20°C for 10 h, further on their cutting in chunks and the drying of rusks for 15 min. at 180° were performed.

Methods of mathematical planning of experiment – central composite rotatable uniform planning – have been used in the work. The processing of experimental data consisted in the check of reproducibility of experiments (Kokhren Criterion), the calculation of coefficients of regression equation and the check of their statistical importance (Student Criterion), the establishment of adequacy of the obtained regression equation (Fischer Criterion) [3, 4].

The following are chosen as the major factors: $x_1$ is the dosage of flour made of wholemeal wheat (wheat germ oil), % to the total mass of flour; $x_2$ is the humidity of dough, % (Table 1). The main indicator of quality of rusks characterizing their swelling capacity in water – the swelling capacity coefficient – was used as the output parameter $y$. The swelling capacity of specimens was determined according to the technique provided in GOST 8494-96, the swelling capacity coefficient was calculated proceeding from an increase in the mass of each specimen after its swelling.

**Table 1. Planning characteristics**

<table>
<thead>
<tr>
<th>Planning conditions</th>
<th>Values of factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dosage of wheat germ oil $x_1$, %</td>
</tr>
<tr>
<td>Basic level (0)</td>
<td>75.00</td>
</tr>
<tr>
<td>Variability range</td>
<td>17.73</td>
</tr>
<tr>
<td>Upper level (+1)</td>
<td>92.73</td>
</tr>
<tr>
<td>Lower level (–1)</td>
<td>57.27</td>
</tr>
<tr>
<td>High &quot;star&quot; point (+1.41)</td>
<td>100.0</td>
</tr>
<tr>
<td>Low &quot;star&quot; point (–1.41)</td>
<td>50.00</td>
</tr>
</tbody>
</table>

The choice of intervals of change of factors was caused by the technical characteristics and quality of the finished products. The addition of wheat germ oil in the amount of less than 50% is inefficient as it does not has a considerable impact on the nutrition value of products. The increase in dough humidity by more than 42.0% provides a decrease in its viscosity and dilution. The semi-finished product with the dough humidity of less than 39.0% has a high viscosity and "abrupt" consistence which complicates its formation and affects the formation of properties of semi-finished products in the course of fermentation, proving and baking.

The optimization of technological parameters of preparation of dough for rusks of high nutrition value was performed using the methods of mathematical statistics and differential calculus.

**RESULTS AND DISCUSSION**

The first stage of work consisted in the identification of parameters of the mathematical model which adequately describes the dependence of output parameter on the studied factors. For these purposes the complete factorial experiment of type $2^3$ according to the planning matrix given in Table 2 has experimentally been made (Experiments 1–4). Each experiment was implemented with two-time replication. Taking into account a possible future transition to second order planning, 5 parallel experiments have been implemented at the center point of the design (Experiments 9–13). To exclude the influence of uncontrollable parameters on the results of experiment the randomization of experiments with the application of the table of random numbers was used. Table 2 provides the arithmetic averages of response function according to the results of two parallel experiments.
Table 2. Planning matrix and results of the experiment

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Code values of factors</th>
<th>Natural values of factors</th>
<th>Response function</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_1$</td>
<td>$X_2$</td>
<td>$x_1, %$</td>
</tr>
<tr>
<td>1</td>
<td>+1</td>
<td>+1</td>
<td>92.73</td>
</tr>
<tr>
<td>2</td>
<td>+1</td>
<td>-1</td>
<td>92.73</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>+1</td>
<td>57.27</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>57.27</td>
</tr>
<tr>
<td>5</td>
<td>+1.41</td>
<td>0</td>
<td>100.0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>+1.41</td>
<td>75.0</td>
</tr>
<tr>
<td>7</td>
<td>-1.41</td>
<td>0</td>
<td>50.0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>-1.41</td>
<td>75.0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>75.0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>75.0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
<td>75.0</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>0</td>
<td>75.0</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>75.0</td>
</tr>
</tbody>
</table>

The application of complete factorial experiment provides the opportunity to calculate the estimates of regression coefficients and to develop a first order equation. It is known [3] that the intercept $b_0$ of regression equation is the estimate of process output at the center point of experiment which is mixed with the total estimate of quadratic effects of all factors. If the quadratic terms are significant, the predicted results of experiments at the center point of the design of experiment will considerably differ from their experimental values, as well. The parallel experiments at the center point of the design of experiment allow, without even starting the calculation of all (except $b_0$) estimates of coefficients of the equation, to judge about the possibility of description of the studied dependence using a first order equation without the inclusion of quadratic terms in it.

In this regard, values of the intercept $b_0$, arithmetic mean values of response function $\bar{y}_0$ at the center point of the experiment, the estimation of difference dispersion $S^2(\bar{y}_0-b_0)$ and the confidential error of difference $\varepsilon$ (Table 3) have been calculated.

Table 3. Results of calculation of confidence error

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept $b_0$</td>
<td>4.93</td>
</tr>
<tr>
<td>Arithmetic average value of response function at the center point of the experiment $\bar{y}_0$</td>
<td>4.8</td>
</tr>
<tr>
<td>Difference-based variance estimate $S^2(\bar{y}_0-b_0)$</td>
<td>$1.3\cdot10^{-3}$</td>
</tr>
<tr>
<td>Difference $</td>
<td>\bar{y}_0-b_0</td>
</tr>
<tr>
<td>Confidence error of difference $\varepsilon$</td>
<td>0.078</td>
</tr>
</tbody>
</table>

The confidence error of difference $\varepsilon$ has been estimated according to the formula

$$\varepsilon = t_{\alpha/2} \cdot \sqrt{S^2(\bar{y}_0-b_0)},$$

where $t_{\alpha/2}$ is the critical value of Student criterion ($t_{0.025} = 2.16$) with the accepted confidential probability of 0.95 and the number of degrees of freedom of 13.

The fulfillment of the condition $\varepsilon < |\bar{y}_0-b_0|$ follows from the results of Table 3. It allows to recognize with the accepted confidential probability of 0.95 the distinction between $\bar{y}_0$ and $b_0$ essential, and to consider the linear regression equation obtained using the results of complete factorial experiment an unsatisfactory mathematical description. In this regard, a decision on the transition to second order planning allowing to obtain the adequate mathematical description due to the inclusion of estimates of quadratic effects of factors in it has been made.

For this purpose, the experiments at the "star" points (Table 2, Experiments 5–8) were added to the planning matrix. The choice of value of "star" leverage ± of 1.41 is caused by the need of obtaining a uniform rotatable design providing the obtaining of the same value of dispersion and the prediction for any point within the studied area. The experiments at the "star" points were realized with two-time replication, as well. Table 2 provides the arithmetic averages of response function according to the results of two parallel experiments.

The statistical processing of results of uniform rotatable planning consisted in the calculation of estimates of coefficients of regression equation, the check of their importance, the estimation of reproducibility of experiments and the establishment of adequacy of the obtained regression equation [3, 5]. Statistical Student, Khokhren and Fischer criteria (with the confidential probability of 0.95) have been used for this purpose.

As a result of statistical processing of results of planning of experiment (Table 2) a regression equation which adequately describes the dependence of swelling...
capacity coefficient of rusks \( y \) on the studied factors has been obtained:
\[
y = 4.8 + 0.39X_1 - 0.35X_2 + 0.15X_1X_2 + 0.23X_1^2 - 0.14X_2^2, \tag{2}
\]
where \( X_i \) is the code values of the factors related to the natural values \( x_i \) with the ratios:
\[
X_1 = \frac{x_1 - 75}{17.73}; \quad X_2 = \frac{x_2 - 41}{2}.
\tag{3}
\]

The second stage consisted in the interpretation of the regression equation (2). The mathematical description obtained using the results of rotatable planning provides the information on the response surface, however, the interpretation of equation in the form of (2) is complicated. In this regard, to establish the type of surface and reduce the equation to the accepted form we will use the means of analytical geometry [6].

For this purpose we will present the regression equation (2) in the form of the general second order surface equation:
\[
a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + 2a_{23}yz + a_0 = 0, \tag{4}
\]
where \( a_0 \) and \( a_{ij} \) are the coefficients of the equation of surface of the second order; \( x, y \) and \( z \) are the variables which correspond to the factors \( X_1 \) and \( X_2 \) and the response function \( y \).

Comparing the regression equation (2) with the general surface equation (4), we determine the coefficients \( a_{0} \) and \( a_{ii} \) (Table 4). Orthogonal invariants of the quadratic function (4) provide the information on the configuration of surface of the second order which is described by the equation (2):

- the determinant \( \delta \) of a matrix of quadratic form
\[
\delta = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & a_{33} \end{vmatrix} = 0.23 \quad 0.075 \quad 0 \quad 0.195, \quad 0.075 \quad -0.14 \quad 0 \quad -0.175, \quad 0 \quad 0 \quad 0 \quad 0 = 0.00946,
\]

- the determinant \( \delta \) of a matrix of quadratic function
\[
\delta = \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_1 \\ a_{12} & a_{22} & a_{23} & a_2 \\ a_{13} & a_{23} & a_{33} & a_3 \\ a_1 & a_2 & a_3 & a_0 \end{vmatrix} = 0.23 \quad 0.075 \quad 0 \quad 0.195, \quad 0.075 \quad -0.14 \quad 0 \quad -0.175, \quad 0 \quad 0 \quad 0 \quad 0 = 0.00946,
\]

We define the coordinates \( X_{1s} = -0.37 \) and \( X_{2s} = -1.45 \) of the stationary point (the center of response surface) which contains the extremum of function (2). The insertion of coordinates of the stationary point in the equation (2) provides the value of response function at the center point of the surface \( y_s = 4.98 \).

Solving the second order characteristic equation
\[
\begin{vmatrix} b_{11} & 1 \\ 1 & b_{22} \end{vmatrix} b_{12} = 0,
\]

we define the coefficients of the accepted form \( B_{11} = 0.25 \) and \( B_{22} = -0.15 \).

### Table 4. Values of coefficients of the general equation of surface of the second order (5)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>( a_{11} )</th>
<th>( a_{22} )</th>
<th>( a_{33} )</th>
<th>( a_{12} )</th>
<th>( a_{13} )</th>
<th>( a_{23} )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>0.23</td>
<td>-0.14</td>
<td>0</td>
<td>0.075</td>
<td>0</td>
<td>0</td>
<td>0.195</td>
<td>-0.175</td>
<td>-0.5</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Thus, the regression equation (2) after canonical transformations has the form

\[ y = 4.98 + 0.25Z_1^2 - 0.15Z_2^2. \]  

(5)

The angle of rotation of the new coordinate axes \( Z_1 \) and \( Z_2 \) of the initial axes \( X_1 \) and \( X_2 \) is

\[ \phi = \frac{1}{2} \arctg \left( \frac{h_2 - h_1}{h_1 - h_2} \right) = 10.9^\circ. \]

Taking into account the parameters of the canonical transformation the relation between the coordinates \( X_i \) and the new \( Z_i \) has the form:

\[
\begin{align*}
X_1 &= (Z_1 + X_1) \cos \phi - (Z_2 + X_2) \sin \phi = 0.982Z_1 - 0.19Z_2 - 0.087, \\
X_2 &= (Z_1 + X_1) \sin \phi + (Z_2 + X_2) \cos \phi = 0.19Z_1 + 0.982Z_2 - 1.494.
\end{align*}
\]

Fig. 1 provides the graphic interpretation of the regression equation (2) in the form of response surface. It is visible that the surface described by the equation (2) the accepted form of which is presented in the form of (5) has the form of a hyperbolic paraboloid with a special central point (the minimax point). In the line of one of the accepted axes there is the minimum and in the line of other axis there is the maximum.

More detailed information on the configuration of response surface is provided by its two-dimensional sections. Fig. 2 provides flat sections of response surface. It is visible that the sections of hyperbolic paraboloid made by the coordinate planes \( y = h \) (where \( h \) is an arbitrary constant) have the form of hyperboles. With \( h < 4.98 \) the half-hyperboles are extended along the accepted axis \( Z_2 \), and with \( h > 4.98 \) the half-hyperboles are extended along the accepted axis \( Z_1 \).

Fig. 2 also presents a two-dimensional section of the area of experiment in the form of a circle with a radius of \( R = 1.41 \) the center of which coincides with the center point of the experiment.

The analysis of two-dimensional sections of response surface allows to determine previously the optimum area of factorial space in which the highest value of output parameter \( y \) is reached. Such a mode (see Fig. 2) obviously corresponds to the vicinities of the right "star" point (according to Table 1 for dosages of wheat germ oil \( x_1 = 100\% \) and the humidity of dough \( x_2 = 41\% \)).

These results are determined by the influence of flour made of wholemeal wheat and the humidity of dough on the formation of properties of semi-finished products and indicators of quality of finished products. It has been revealed that with an increase in the dosage of flour made of wholemeal wheat and a decrease in the humidity of dough the swelling capacity coefficient of rusk s increases. Its highest value has been noted when adding the maximum amount of wheat germ oil and humidity of dough at the center point of the design (Fig. 2). The existence of considerable amounts of peripheral parts of grain (food fibers) with a high water absorbing ability in such flour is determinative. The mass of water retained by 1 g of flour made of wholemeal wheat is 1.27 g compared to 0.85 g for high-grade wheat flour.

**The third stage** consisted in the optimization of dough formulation in the value of swelling capacity coefficient of rusk s \( y \).

We will formulate the problem of optimization of technological parameters of preparation of dough for rusk s of high nutrition value as follows. It is necessary...
to determine such values of the variables \( X_1 \) and \( X_2 \) which provide the maximum value of the swelling capacity coefficient \( y = y(X_1, X_2) \). At the same time the values of the variables \( X_1 \) and \( X_2 \) are also to be in the area of experiment the borders of which are determined by the values of factors at the "star" points.

We will present the specified restriction imposed on the variables \( X_1 \) and \( X_2 \) in the form of

\[
\begin{align*}
\phi(X_1, X_2) &= X_1^2 + X_2^2 = R^2, \\
y(X_1, X_2) &= 4.8 + 0.39X_1 - 0.35X_2 + 0.15X_1X_2 + 0.23X_1^2 - 0.14X_2^2 \rightarrow \text{max}
\end{align*}
\]

We will solve the problem of conditional optimization using the method of Lagrange multipliers [7] which allows to reduce the problem of conditional optimization to an unconditional problem of search of function extremum.

\[
F(X_1, X_2, \lambda) = 4.8 + 0.39X_1 - 0.35X_2 + 0.15X_1X_2 + 0.23X_1^2 - 0.14X_2^2 + \lambda(X_1^2 + X_2^2 - R^2).
\]

A necessary condition of unconditional extremum of Lagrange function \( F(X_1, X_2, \lambda) \) is the equality of differential derivatives of function (8) to zero by all the independent variables \( X_1 \), \( X_2 \) and an uncertain multiplier \( \lambda \):

\[
\begin{align*}
\frac{\partial F(X_1, X_2, \lambda)}{\partial X_1} &= 0.39 + 0.15X_1 + 0.46X_2 + 2\lambda X_1 = 0, \\
\frac{\partial F(X_1, X_2, \lambda)}{\partial X_2} &= -0.35 + 0.15X_1 - 0.28X_2 + 2\lambda X_2 = 0, \\
\frac{\partial F(X_1, X_2, \lambda)}{\partial \lambda} &= X_1^2 + X_2^2 - R^2 = 0.
\end{align*}
\]

To solve the system of equations (9) it is necessary to assign the values of the radius \( R \) in the range from 0 to 1.41. However, as it follows from Fig. 2, the conditional extremum of coefficient of swelling of ruskys \( y = y(X_1, X_2) \) is reached under the condition \( R = 1.41 \). In this regard the problem of optimization is considered in future for the case \( R = 1.41 \).

Solving the system (9) referring the variables \( X_1 \), \( X_2 \) and the Lagrange multiplier \( \lambda \), we obtain the values \( \lambda^* \) and coordinates of stationary points of factorial space \( X_1^* \) and \( X_2^* \) at which the conditional extremum of function is reached (2) (Table 5). It is not difficult to see that the coordinates of each extreme point satisfy the constraint equation (6).

The condition (9) is a necessary condition for the existence of Lagrange function extremum (8), but not a sufficient one. To check the sufficient condition for the existence of the found extrema and the establishment of their character we will use a matrix

\[
H = \begin{pmatrix}
0 & \frac{\partial \phi}{\partial X_1} & \frac{\partial \phi}{\partial X_2} \\
\frac{\partial \phi}{\partial X_1} & \frac{\partial^2 F}{\partial X_1^2} & \frac{\partial^2 F}{\partial X_1 \partial X_2} \\
\frac{\partial \phi}{\partial X_2} & \frac{\partial^2 F}{\partial X_2 \partial X_1} & \frac{\partial^2 F}{\partial X_2^2}
\end{pmatrix}
\]

which is generated using the differential derivatives \( \frac{\partial \phi}{\partial X_i} \) of the constraint equation (6) and the Hessian matrix

\[
\begin{pmatrix}
\frac{\partial^2 F}{\partial X_1^2} & \frac{\partial^2 F}{\partial X_1 \partial X_2} \\
\frac{\partial^2 F}{\partial X_2 \partial X_1} & \frac{\partial^2 F}{\partial X_2^2}
\end{pmatrix}
\]

Table 5. Results of optimization

<table>
<thead>
<tr>
<th>Point No.</th>
<th>( X_1^* )</th>
<th>( X_2^* )</th>
<th>( \lambda^* )</th>
<th>( \text{det} H )</th>
<th>Constraint extremum functions</th>
<th>( y, \text{ c.u.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.55</td>
<td>1.30</td>
<td>0.31</td>
<td>-8.57</td>
<td>min</td>
<td>3.86</td>
</tr>
<tr>
<td>2</td>
<td>-0.44</td>
<td>-1.34</td>
<td>-0.016</td>
<td>-2.12</td>
<td>min</td>
<td>4.98</td>
</tr>
<tr>
<td>3</td>
<td>-0.99</td>
<td>-1.00</td>
<td>-0.11</td>
<td>2.18</td>
<td>max</td>
<td>5.0</td>
</tr>
<tr>
<td>4</td>
<td>1.40</td>
<td>-0.14</td>
<td>-0.36</td>
<td>7.62</td>
<td>max</td>
<td>5.82</td>
</tr>
</tbody>
</table>
Inserting all the differential derivatives in the matrix (10), we will generate its determinant

$$\text{det} H = \begin{vmatrix} 0 & 2X_1 & 2X_2 \\ 2X_1 & (0.46 + 2\lambda) & 0.15 \\ 2X_2 & 0.15 & (-0.28 + 2\lambda) \end{vmatrix}. \quad (11)$$

For each found stationary point with the coordinates \((X'_1, X'_2, \lambda')\) we calculate the value of determinant of the matrix \(H\) (Table 5) using the formula (11). It is visible that the matrix \(H\) is negatively certain for the first two stationary points (since \(\text{det} H < 0\)), therefore, for these points, the second order differential of the Lagrange function \(d^2F > 0\) and, thus, these points are the points of conditional minimum. For other stationary points, the matrix \(H\) is positively certain, the second order differential of the Lagrange function \(d^2F < 0\), therefore, the required stationary points are the points of conditional maximum. The values of optimization parameter \(y\) at the established stationary points of factorial space are calculated using the equation 2 and are presented in Table 5.

The results of optimization are in full accordance with the configuration of response surface. Thus, the first two stationary points with the coordinates \((-0.55; 1.3)\) and \((-0.44; -1.34)\) respectively are located on the descending half-hyperbole paraboloids (see Fig. 2). Therefore, the specified points are classified as the points of conditional minimum of the optimization (7), the parameters of doughing \(X'_1 = 1.4\) and \(X'_2 = -0.14\) which provide the obtaining of rusks with the maximum value of swelling capacity coefficient, \(y = 5.82\) c.u., should be considered as rational ones.

Thus, proceeding from the formulated condition of optimization (7), the parameters of doughing \(X'_1 = 1.4\) and \(X'_2 = -0.14\) those which provide the obtaining of rusks with the maximum value of swelling capacity coefficient, \(y = 5.82\) c.u., should be considered as rational ones.

The transition from code values of factors to natural ones taking into account the characteristics of planning (see Table 1) allows to obtain rational values of dosage of wheat germ oil \(x_1 = 99.82\%\) and humidity of dough \(x_2 = 40.86\%\).

The fourth stage consisted in the estimation of reliability and degree of accuracy of the obtained value of optimization criterion. Dispersion of prediction of the value of optimization parameter [3]

$$S^2(y) = S^2_{b_0} + S^2_{b_1}R^2 + S^2_{b_2}R^4 + 2\text{cov}_{b_1b_2}R^2, \quad (12)$$

where \(S^2_{b_0}, S^2_{b_1}\) and \(S^2_{b_2}\) are the dispersions when determining the regression coefficients \(b_0, b_1\) and \(b_2\) respectively; \(\text{cov}_{b_1b_2}\) is covariance; \(R\) is the radius of the sphere with a point of the optimum values of factors \(X'_1 = 1.4\) and \(X'_2 = -0.14\) \((R = 1.41)\).

Dispersion when determining regression coefficients are related to residual dispersion and constants of dispersion matrix by the known ratios. Error of prediction of value of optimization criterion

$$\delta = t_{fp} \sqrt{S^2(y)}, \quad (13)$$

where \(t_{fp}\) is the critical value of Student criterion \((t_{fp} = 2.37\) with the significance value \(p = 5\%\) and the number of degrees of freedom \(f = 7)\).

Table 6 provides the results of calculations of dispersion of prediction \(S^2(y)\) of the optimization parameter and its confidential interval \(y \pm \delta\) (with the confidential probability of 0.95).

The objectivity of determination of rational values of parameters of preparation of dough is confirmed by the results of parallel experiments that show sufficient convergence of results. The average square error did not exceed 0.67%.

**CONCLUSION**

On the basis of the obtained data a formulation and a way of production of rusks of high nutrition value "Crackling delicacy" has been developed. As for the organoleptic and physical and chemical indicators of quality, the products do not concede the traditional ones, and as for the content of protein, food fibers, mineral substances and vitamins they considerably surpass them (Table 7). Technical documentation (TU 9110-394-02068108-2017) has been developed for the enriched product.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimum value of criterion of optimization, c.u.</td>
<td>5.82</td>
</tr>
<tr>
<td>Dispersion (S^2(y))</td>
<td>0.08</td>
</tr>
<tr>
<td>Prediction error (\delta), c.u.</td>
<td>0.67</td>
</tr>
<tr>
<td>Confidential interval (y \pm \delta), c.u.</td>
<td>5.82 ± 0.67</td>
</tr>
</tbody>
</table>
Table 7. Characteristics of nutrition value of dry bread products

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Daily rate for the adult (according to TR TS 022/2011)</th>
<th>Children's rusks (control)</th>
<th>Rusks &quot;Crackling delicacy&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Contents in 100 g of the product</td>
<td>Degree of satisfaction of daily requirement, %</td>
</tr>
<tr>
<td>Proteins, g</td>
<td>75</td>
<td>9.6</td>
<td>13</td>
</tr>
<tr>
<td>Fats, g</td>
<td>83</td>
<td>2.9</td>
<td>3</td>
</tr>
<tr>
<td>Carbohydrates, g</td>
<td>365</td>
<td>74.9</td>
<td>21</td>
</tr>
<tr>
<td>Food fibers, g</td>
<td>30</td>
<td>3.1</td>
<td>10</td>
</tr>
<tr>
<td>Potassium, mg</td>
<td>3500</td>
<td>108</td>
<td>3</td>
</tr>
<tr>
<td>Calcium, mg</td>
<td>1000</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>Phosphorus, mg</td>
<td>800</td>
<td>76</td>
<td>9</td>
</tr>
<tr>
<td>Magnesium, mg</td>
<td>400</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>Iron, mg</td>
<td>14</td>
<td>1.3</td>
<td>9</td>
</tr>
<tr>
<td>Vitamin B₁, mg</td>
<td>1.4</td>
<td>0.14</td>
<td>10</td>
</tr>
<tr>
<td>Vitamin B₂, mg</td>
<td>1.6</td>
<td>0.02</td>
<td>1</td>
</tr>
<tr>
<td>Vitamin PP, mg</td>
<td>18</td>
<td>1.05</td>
<td>6</td>
</tr>
<tr>
<td>Vitamin E, mg</td>
<td>10</td>
<td>0.85</td>
<td>9</td>
</tr>
<tr>
<td>Caloric value, kcal / kJ</td>
<td>2500/10467</td>
<td>364/1524</td>
<td>15</td>
</tr>
</tbody>
</table>

REFERENCES


INNOVATIVE ENCAPSULATION TECHNOLOGY OF FOOD SYSTEMS USING A BY-PRODUCT OF DAIRY PRODUCTION

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Abstract: Currently, promising innovative direction in the food production technology is the use of techniques of "molecular gastronomy", allowing to modify the consumer properties of traditional foods. One of the techniques of this direction is the technology of "spherification" – the process of encapsulation of various food masses (sauces, juices, extracts, etc.). This technology will allow not only to use it as a tool of innovative management in the restaurant business, but also to expand the field of application of encapsulation in connection with the use of structure-forming agents of domestic production and by-products of the dairy industry. The purpose of the study was to investigate the influence of various factors on the process of encapsulation of food masses: generation of alginate shell when using curd whey as a capsule-forming medium. Methods of instrumental analysis are used in the work. Determination of the qualitative composition and identification of the test ingredients for encapsulation was carried out by IR-Fourier spectrometry. Capsules were prepared by axially feeding into the curd whey of sodium alginate solutions through a device for producing encapsulated products with a fixed size of the nozzle outlets. The results of determining the qualitative composition of the binary system "sodium alginate – curd whey" presumably indicate the complexation of polymers present in the system. It was found that in order to obtain a capsule shape close to a roundly regular one, the concentration of sodium alginate in the encapsulated solution should be between 0.8% and 1.2%. With an increase in the outlet diameter, and also with an increase in the concentration of the structure-forming agent in the encapsulated solution, an increase in the diameter of capsules was observed. The diameter of capsules obtained under the given conditions ranged from 3.7 to 5.7 mm. Generalization of the experiment results served as the basis for developing the technology of encapsulated food products based on the "spherification" method by diffusion of the cross-linking ion (Ca2+) from an external reservoir (curd whey) into a capsular liquid containing sodium alginate. Process conditions for the production of encapsulated food products with specified consumer properties have been established.

Keywords: Capsulation, sodium alginate, milk whey, calcium alginate

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INTRODUCTION

One of the innovative directions in the technology of catering production is the use of "molecular gastronomy" techniques, based on scientific knowledge of the properties of food products and the possibility of modifying their consumer properties [1].

With the advent of "molecular gastronomy," the technological properties of little-known hydrocolloids became more applicable for catering producers, which influenced the expansion of their use in the development of innovative food products [2, 3]. One of the methods of this direction is encapsulation of various food masses (sauces, juices, extracts, etc.).

In the food industry, the use of encapsulation technology is due to a variety of reasons. This method is an effective tool for delivering biologically active molecules (antioxidants, minerals, vitamins, phytosterols, polyunsaturated fatty acids, etc.) and living cells (probiotics) into food [4–6].

Encapsulation is the process of incorporating one material into a shell made of another material to produce particles ranging in size from several nanometers to several millimeters, in other words, immobilizing solid, liquid or gaseous substances into capsules that release the contents at a controlled rate for a predetermined period of time under certain...
environment conditions. The substance that is encapsulated is called the active substance, or the main product, or internal phase. The material into which the main product is enclosed is called a shell, a membrane, a wall, an outer phase, or a matrix [7–11].

The following substances are used as membrane material for encapsulation: Hydrogels (agar-agar, k-carrageenan, alginates, chitosan, cellulose, etc.), proteins (collagen, gelatin, chicken egg whites, fibrin, etc.), synthetic polymers (polyacrylamide, polyvinyl alcohol, polyethylene glycol methacrylate, polyisocyanates, polyurethane, etc.), etc. Based on the desired characteristics of the finished capsules, it is possible to select a particular substance for encapsulation [12–14].

Alginates are one of the most preferred ingredients for use in encapsulation technology. They are widely distributed in nature as a structural component of brown algae [15]. The safety of alginic acid and its ammonium, calcium, potassium and sodium salts was established by the Joint Expert Committee on Food Additives (JECFA) in 1992 [16].

Alginates are a family of unbranched binary copolymers formed by the residues of β-D-mannuronic acid (M) and α-L-guluronic acid (D), connected by a (1→4)-bond, which vary greatly in composition and sequence. The composition and structure of the sequence may vary depending on the season and growth conditions, as well as the part of the plant from which the structure-forming agent was obtained. The distribution of monomer residues of these acids along the polymer chain has a block character and forms three types of blocks:

- Homopolymer blocks of monotonic sequences of β-D-mannuronic acid residues (M-blocks);
- Homopolymer blocks of monotonic sequences of α-L-guluronic acid residues (H-blocks);
- Heteropolymer blocks with alternation of residues of both acids (M-H-blocks).

Such a structure of polymer molecules leads to formation of crystallinity zones in H-blocks, amorphous regions (flexibility zones) in M-blocks and areas with intermediate rigidity in heteropolymer M-H-blocks [17, 18].

Alginic acid salts are classified as high molecular weight water-soluble compounds used in the food industry as a structure-forming agent [19].

Alginates are thermostable compounds. The viscous properties of alginate remain in a wide range of temperatures. The viscosity of alginate solutions decreases by approximately 12% with temperature increase by every 5.6°C. These changes are reversible, solutions acquire initial viscosity upon cooling again. However, as a result of high thermal effects (above 95°C), destruction of the alginate molecule and the weakening of the van der Waals cohesion forces in the dispersion medium occur, which leads to a complete loss of aggregative gel stability, combination of colloidal particles in large aggregates, and formation of a dense precipitate, coagulate [20, 21].

Alginates have an important ability to bind ions, which is the basis of their gel-forming properties. The affinity of alginates for alkaline earth metals increases in the following order: Mg$^{2+}$ < Ca$^{2+}$ < Sr$^{2+}$ < Ba$^{2+}$. This unique property of alginates distinguishes them from other polyanions. The only polyanion resembling alginates from this point of view is pectic/pectinic acid, whose affinity follows the scheme Mg < Ca, Sr < Ba [22]. In the absence of a bivalent cation (Ca$^{2+}$, Mg$^{2+}$), alginates only increase the viscosity of the solutions in proportion to the concentration of the structure-forming agent. However, when a multivalent cation is added, especially calcium and at a low pH (≤ 4), a gel is formed. The molecules in this case will be crosslinked by polyvalent ions (the "egg box" model). As the acidity of the solution decreases, the charge of dispersed particles decreases, and the forces of attraction begin to predominate over the repulsive forces. The residues of guluronic acid form a curved conformation, which ensures effective binding of cations (Fig. 1) [23, 24].

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**Fig. 1.** Structural characteristics of alginates: (a) M: β-D-mannuronate, G: α-L-guluronate; (b) chain conformations; (c) block distribution.
In solving problems associated with gelation of sodium alginate, the determining property is the ability to regulate the introduction of cross-linking ions. This control can be carried out using two basic methods of preparing an alginate gel: method of diffusion and method of internal gel formation. The first method is characterized by diffusion of a cross-linking ion from the external reservoir into the alginate solution. Internal gel formation (sometimes called gelling in the block (in situ)) differs from the previous method in that Ca$^{2+}$ ions release from an inert calcium source in an alginate solution in a controllable way. Controlled release is usually achieved by changing pH level and/or by a limited source solubility of the calcium salt [25].

Ferran Adrià, chef at the El Bulli restaurant, became the pioneer of encapsulation technology in public catering, using the ability of alginate solutions to form gels by adding Ca$^{2+}$ ions to them. In gastronomic circles, this method was termed “spherification” [26, 27]. The spherification technology consists in applying the diffusion method. The essence of the method consists in the interaction of sodium alginate with a bivalent cation, for example, a calcium ion or other polyvalent metal (zinc, aluminum, copper), to form a gel. Diffusion formation of the gel structure is characterized by a high gel formation rate, and this high-speed curing is used as a method of immobilizing and restructuring food products. Each drop of the alginate solution forms one granule of gel with the inclusion of the active agent. The spatial grid of the gel is formed by the interaction of calcium ions with carboxyl groups and additionally stabilized by coordination links between calcium ions and hydroxyl groups, hyaluronic acid residues (Fig. 2) [22].

A feature of the diffusion gel formation process is that the resulting gel is characterized by an inhomogeneous distribution of alginate with its high concentration on the surface, which gradually decreases towards the center of the gel. This phenomenon is explained by the fact that during the diffusion process a gelation zone is formed, which moves from the surface to the center of the gel. The alginate activity in this zone is zero, and the alginate molecule diffuses from the internal, unstructured part of the system, passing into the gel, into the zone of zero activity [28, 29].

This process of formation of alginate gels is used to produce spheres of small size with a dense shell and a liquid center. The product obtained in this way has the texture and appearance of natural fish caviar, and at the same time it has a different flavor and taste [30].

For the implementation of the spherification technology, a solution is prepared based on sodium alginate and liquid filler with projected taste. Introduction of the encapsulated mixture is carried out by axial dropping into a prepared solution containing calcium ions, and an instantaneous formation of a spherical shell around the encapsulated substance takes place. One of the striking examples of the use of this technique in the restaurant El Bulli is the production of spherical green "olives", which are served on a special spoon [30].

In the original procedure for the implementation of the spherification method, the concentration of alginate in the encapsulated solution is from 0.6 to 4%, the content of calcium chloride in the forming solution varies from 0.05 to 1.5 mole. Thus, it is possible to obtain spherical capsules with a diameter of 0.2 to 5 mm depending on the instrumentation used (pipette, syringe, oscillating nozzle, spray nozzle, coaxial air flow, electric field, etc.) and viscoelastic characteristics of the encapsulated solution of sodium alginate [5].

In studying this encapsulation technology, scientists have found that the rate of gel formation of sodium alginate solutions is the highest when using calcium chloride as a calcium-containing component. Compositions based on gluconate or calcium lactate have the least gel-forming ability. Alginate capsules formed by keeping them in a solution of calcium chloride acquire the maximum strength characteristics after 100 seconds of droplet retention in the forming solution, while in order to achieve such characteristics, capsules in a calcium lactate solution require a holding time of 500 seconds, calcium gluconate – of 3000 seconds.

Based on the application of the Tate law, a model was developed to predict the shape and size of alginate granules in the range from 2.9 to 3.25 mm produced by the drop method [31].

An alternative to "suppliers" of calcium ions (calcium chloride, lactate and gluconate) is milk whey, which is a by-product of cheese production, or casein, and is not widely used for commercial purposes, and often simply recyclable. Milk whey is close to natural cow milk in its composition [32] and is rich in physiologically valuable whey proteins, water-soluble vitamins and lactose. There are two types of milk whey: curd (sour) and cheese (sweet).

The choice of curd whey as a calcium-containing component with the application of encapsulation technology by the method of spherification is due to the high content of calcium in it as compared with the cheese whey [33]. Inclusion of curd whey in the composition of the shell increases the nutritional value of a capsule, and its application in the production of
encapsulated food products seems to be a promising direction.

The purpose of the study was to review the process of the formation of sodium alginate when using by-products of dairy production as a calcium-containing component for encapsulation of food masses.

OBJECTS AND METHODS OF STUDY

Sodium alginate (TU 15-544-83 "Sodium alginate food") and curd whey (GOST R 53438-2009 "Dairy whey. Specifications") were used as the objects of the study.

For the preparation of binary systems "sodium alginate – curd whey", a sample of sodium alginate was injected into the curd whey solution, dispersed at a temperature of 20 to 22°C for 60 minutes with a magnetic stirrer. The resulting solution was dried in a Vac Modul vacuum module, with a vacuum pump VP1, for VD 53 to a moisture mass fraction in the sample of 15%.

To prepare model solutions to be encapsulated, a sample of sodium alginate was dispersed in a mixture of curd whey and water taken at a ratio of 50 : 50 at a temperature of 20 to 22°C for 3–4 minutes on a magnetic stirrer. The resulting solution was placed in a refrigerated cabinet at a temperature of from 2 to 6°C for degassing the solution for 3 hours.

Capsules were produced by axial feeding into the curd whey of sodium alginate solutions through the device for producing encapsulated products [Patent RF 156197] with a fixed size of nozzle outlets. Injection of drops of the extrusion mixture in the form of a sodium alginate solution into the forming medium – curd whey – was carried out at a ratio of 1 : 10. Spheres were obtained differing in their structural and mechanical characteristics and dimensional parameters, due to the diffuse structure formation occurring over time. To maintain a constant amount of Ca²⁺ ions in the whey, its solution was constantly freshened. The finished capsule cores were washed with distilled water and dried on filter paper. The experimental setup layout is shown in Fig. 3.

Determination of the qualitative composition and identification of dry powders taken as the objects of the study was carried out by IR-Fourier spectrometry with an Agilent Cary 660 spectrometer.

Spectra were interpreted using literature data [34].

To determine the dimensional characteristics of the resulting capsules, a XSP 10-640x microscope with a MOV-1-16x screw micro-eyepiece with a measurement scale with measurement limits from 0 mm to 8 mm was used.

The capsule shape factor was determined by the formula [35]:

\[ K_f = \pi \left( \frac{a}{b} \right) \left( \frac{b}{a} \right) \]

where \( a \) and \( b \) are semi-axes of the ellipse, mm.

The minimum possible value \( K_f \) has the circle (\( K_f = 2\pi \)).

RESULTS AND DISCUSSION

The analysis of the patent information literature and comparative characteristic of the physico-chemical properties of sodium alginate and curd whey composition allowed to formulate the main scientific approaches to the development of encapsulation technology for food systems.

For the scientific substantiation of the use of alginates as a membrane-building material, it is necessary to establish the effect of certain process factors on the characteristics of the gels formed. The most important factors are:

- Concentration of alginate;
- Interaction of calcium ions of curd whey with carboxyl groups of sodium alginate and the ratio between gel-forming and gel-non-forming ions;
- Presence of complexing agents (phosphates, citrate, EDTA, GDL, acids).

In determining the qualitative composition and identifying the ingredients used in the encapsulation technology, the IR spectra of the study objects were obtained: curd whey, sodium alginate and binary system "sodium alginate – curd whey".

The presence of a broad absorption band in the 3600-3100 cm⁻¹ region was established in the IR spectra of the curd whey sample, which indicates the presence of valence vibrations of hydroxyl groups (OH) and amino groups (NH) in the molecule (Fig. 4). The presence of absorption bands of 1650 cm⁻¹ and 1550 cm⁻¹ is due to valence vibrations of the C=O bond and to plane deformation vibrations of the NH bond. Thus, it is confirmed that a protein group is present in the analyte.

The IR spectrum of a sodium alginate sample coincides with the spectrum of a known ingredient recorded in the instrument library (Fig. 5). In the test sample in the 3500–3000 cm⁻¹ region, absorption bands
due to stretching vibrations of hydroxyl group are observed, in the region of 2800–3000 cm\(^{-1}\), there are bands of valence vibrations of CH groups, in the region of 1000–1100 cm\(^{-1}\), there are vibration bands of pyranose cycles, absorption bands at 1650–1550 cm\(^{-1}\) are typical for the ionized carboxyl groups of which hydrogen ions are replaced by sodium, which in turn when adding whey will be presumably substituted for the calcium ion, due to the greater reactivity of the latter.

To confirm this assumption on the interaction of study objects, a spectrum of the binary system "sodium alginate – curd whey" was obtained. The presence of absorption bands in the 1950–2150 cm\(^{-1}\) region indicates the presence of C=N=N valence bonds (Fig. 6), and the valence vibrations of hydroxyl groups (OH) and amino groups (NH) in the composition under study (Table 1). This fact presumably indicates the complexation of polymers present in the system.

Fig. 4. IR spectra of a curd whey sample.

Fig. 5. IR spectra of a sodium alginate sample.

Fig. 6. IR spectra of a binary system sample based on decalcified curd whey and sodium alginate.
Table 1. Assignment of absorption bands in IR spectra of curd whey and sodium alginate before and after interaction

<table>
<thead>
<tr>
<th>Wave number, cm⁻¹</th>
<th>Bands assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium alginate</td>
<td>curd whey &quot;sodium alginate-curd whey&quot;</td>
</tr>
<tr>
<td>1000–1100</td>
<td>Vibration bands of pyranose cycles</td>
</tr>
<tr>
<td>1260</td>
<td>Flat deformation vibrations of OH groups in structures</td>
</tr>
<tr>
<td>1380</td>
<td>Scissor vibrations of OH groups, CH₂</td>
</tr>
<tr>
<td>1550–1650</td>
<td>Presence of valence vibrations of the C=O bond and</td>
</tr>
<tr>
<td></td>
<td>plane deformation vibrations of the NH bond</td>
</tr>
<tr>
<td>1600–1650</td>
<td>Presence of C=N=N valence bonds</td>
</tr>
<tr>
<td>1950–2050</td>
<td>Bands of valence vibrations of CH groups</td>
</tr>
<tr>
<td>2800–3000</td>
<td>Presence of valence vibrations of hydroxyl groups (OH)</td>
</tr>
<tr>
<td>3000–3500</td>
<td>and amino groups (NH) in the molecule</td>
</tr>
</tbody>
</table>

To predict the shape and size of the alginate capsules, the influence of various process parameters was studied through a two-factor experiment, planned with the help of Box-Hunter's rotational second-order plans.

As considered factors, presumably having an effect on the diameter of the capsules, the following were accepted: mass fraction of sodium alginate in the encapsulated solution in the range from 0.6 to 1.4% (factor \( X_1 \)), the outlet diameter is from 1 mm to 5 mm (factor \( X_2 \)) (Table 2).

The results obtained during the experiment and data processing is presented in Table 3.

As a result of the regression-correlation analysis, an array of data was obtained reflecting the general regression equation showing the relationship between the diameter of the finished capsules and encapsulation parameters under consideration: outlet diameter, mass fraction of sodium alginate

\[
Y = 0.225 + 5.938 \cdot X_1 + 0.313 \cdot X_2 - 3.281 \cdot X_1^2 - 0.081 \cdot X_2^2 + 0.625 \cdot X_1 \cdot X_2,
\]

The obtained results allow to draw a conclusion that, according to the degree of influence on the diameter of the finished capsules, the factors considered can be arranged in descending order: concentration of sodium alginate injected–outlet diameter (Fig. 7).

Table 2. Values of factors in natural and non-dimensional scales

<table>
<thead>
<tr>
<th>Name of factors</th>
<th>Possible values</th>
<th>–1.414</th>
<th>–1</th>
<th>0</th>
<th>+1</th>
<th>+1.414</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_1 ) – amount of sodium alginate injected, %</td>
<td>0.6</td>
<td>0.7</td>
<td>1.0</td>
<td>1.3</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>( X_2 ) – outlet diameter, mm</td>
<td>1.0</td>
<td>1.6</td>
<td>3.0</td>
<td>4.4</td>
<td>5.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Experiment results

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>( X_1 ) – amount of sodium alginate injected, %</th>
<th>( X_2 ) – outlet diameter, mm</th>
<th>Y value is the capsule diameter, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8</td>
<td>1.6</td>
<td>4.2</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>1.6</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>4.4</td>
<td>4.6</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>4.4</td>
<td>5.4</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>3.0</td>
<td>4.9</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>5.0</td>
<td>5.7</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>1.0</td>
<td>3.7</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>11</td>
<td>1.0</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>12</td>
<td>1.0</td>
<td>3.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Preparation of the desired capsule shape (sphere) with the optimum ratio of the shell thickness to the diameter of the contents is mainly dependent on the viscosity of the encapsulated solution. It is determined that in order to obtain a capsule shape approximating to a roundly regular one, the necessary concentration of sodium alginate in the encapsulated solution should be from 0.8 to 1.2%. As the concentration of the structure-forming agent and, consequently, viscosity of the encapsulated system increases, the shape of the capsules differs from the spherical and approaches it to the elliptical. Reducing concentration of structure-forming agent below the optimal value leads to an increase in the residence time of the capsules in the forming solution, as well as to deformation during their extraction from the curd whey solution.

An increase in the diameter of the capsules is observed with an increase in the concentration of the structure-forming agent in the encapsulated solution and with an increase in the outlet diameter. The diameter of the resulting capsules under given conditions varies from 3.7 to 5.7 mm. At a low concentration of sodium alginate, the axial feed of the solution to the curd whey is not easily implemented, which leads to impossibility of controlling consumption of the filler material of the capsules. This pattern is also observed with an increase in the outlet diameter. Generalization of the experiment results served as the basis for developing the technology of encapsulated food products by the method of "spherification" based on the gelling of sodium alginate with the calcium-containing component – curd whey.

The encapsulation technology involves extrusion of a capsule mixture containing 1% sodium alginate by axial feeding into a forming solution (curd whey) through a 3-mm diameter outlet (Table 4). In this way, spherical capsules of round-regular shape with a diameter of 5 mm and high organoleptic parameters are obtained.

The proposed technology is tested in production conditions, a sweet dish is prepared: a lemon starch drink, containing a capsular side dish based on raspberry juice and tarragon extract.

Implementation of the developed technology in the food industry will expand the range of innovative culinary products that will increase the competitiveness of industry enterprises.

ACKNOWLEDGEMENTS

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Table 4. Process parameters of production of capsular side dish by the "spherification" method

<table>
<thead>
<tr>
<th>Process stage and process mode</th>
<th>Process mode value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Preparation of the liquid to be spherified</td>
<td></td>
</tr>
<tr>
<td>1.1 Neutralization of curd whey (to pH ≥ 4.2)</td>
<td></td>
</tr>
<tr>
<td>amount of acidity regulator, %</td>
<td>1.5</td>
</tr>
<tr>
<td>1.2 Dissolution of sodium alginate</td>
<td></td>
</tr>
<tr>
<td>concentration, %</td>
<td>1</td>
</tr>
<tr>
<td>volume of decalcified curd whey, %</td>
<td>67.5</td>
</tr>
<tr>
<td>volume of encapsulated ingredient, %</td>
<td>30</td>
</tr>
<tr>
<td>structure-forming agent expanding, min</td>
<td>40</td>
</tr>
<tr>
<td>1.3 Mixing of prepared components</td>
<td></td>
</tr>
<tr>
<td>mixing type</td>
<td>manual/auto</td>
</tr>
<tr>
<td>time, sec</td>
<td>30</td>
</tr>
<tr>
<td>2. Solution degassing</td>
<td></td>
</tr>
<tr>
<td>cooling, °C</td>
<td>4 ± 2</td>
</tr>
<tr>
<td>time, min</td>
<td>30</td>
</tr>
<tr>
<td>3. Preparation of the forming solution</td>
<td></td>
</tr>
<tr>
<td>curd whey thermostating</td>
<td></td>
</tr>
<tr>
<td>time, min</td>
<td>30</td>
</tr>
<tr>
<td>temperature, °C</td>
<td>20–22</td>
</tr>
<tr>
<td>4. Encapsulation</td>
<td></td>
</tr>
<tr>
<td>ratio of the encapsulated mixture to the forming solution, g/g</td>
<td>1 : 10</td>
</tr>
<tr>
<td>dynamic viscosity of the encapsulated solution, cP</td>
<td>280–1000</td>
</tr>
<tr>
<td>outlet diameter, mm</td>
<td>3</td>
</tr>
<tr>
<td>capsule diameter, mm</td>
<td>5</td>
</tr>
<tr>
<td>capsule residence time in the forming solution, sec</td>
<td>120</td>
</tr>
<tr>
<td>5. Spheres washing</td>
<td></td>
</tr>
<tr>
<td>capsule-water ratio, g/g</td>
<td>1 : 4</td>
</tr>
<tr>
<td>time, sec</td>
<td>30</td>
</tr>
<tr>
<td>6. Capsule drying</td>
<td>until moisture removal from the surface</td>
</tr>
</tbody>
</table>

REFERENCES

ANALYSIS OF INFLUENCE OF BIOHUMUS ON THE BASIS OF CONSORTIUM OF EFFECTIVE MICROORGANISMS ON THE PRODUCTIVITY OF WINTER WHEAT

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Abstract: The article considers the problem of recycling of poultry waste, in particular, feather-downy waste and chicken dung. Traditional ways of poultry waste disposal have been shown and their shortcomings have been described. The main advantages of use of bioproducting methods to implement the process of waste conversion with the formation of effective products — biohumus — have been determined. Biofertilizers or biohumus is a modern innovative means applied not only for the purpose of an increase in productivity, but also for land recultivation and resuscitation. The authors have studied the biohumus obtained by means of processing of mixture of feather-downy waste and dung in the ratio of 8:2 with the application of the biological product containing the consortium of decomposer microorganisms: Bacillus pumilus AL16, Microbacterium terregens AC1180, Aeromonas sp. B5376, Arthrobacter globiformis AC1529, Streptomyces olivocinerus AC1169 and Acinetobacter sp. B390. An assessment of efficiency of application of various rates of the developed biohumus for winter wheat crops has been made. It is shown that the application of a comparison sample - the organic mineral fertilizer "Universal'noe" (the expense is 150 g/m\textsuperscript{2}) and the use of the developed biohumus (the expense is 150 g/m\textsuperscript{2}) provided an increase in its growth, compared with the control sample of the wheat "Skipetr", by 12 and 15 cm (the stem elongation stage), by 15 and 18 cm (the earing stage), by 21 and 30 cm (the milk stage) and by 19 and 30 cm (the firm ripe stage) respectively. The above values for the grade Zimushka were within the similar limits: an increase in its growth, compared with the control sample, by 17 and 18 cm (the stem elongation stage), by 19 and 21 cm (the earing stage) and by 19 and 31 cm (the milk stage and the firm ripe stage) respectively. An increase in the productivity of grades of the winter wheat "Skipetr" and "Zimushka" by 1.5 times (1.25 ± 0.25 t/hectare) has been established during the application of the obtained biohumus with the rate of 150 g/m\textsuperscript{2}. The results of studies of change of fractional composition of grain proteins testify that the application of biohumus provides an increase in gluten fractions of winter wheat grains. An assessment of economic efficiency has been performed, it has been established that the highest rates of profitability refer to the variant with the application of the developed biohumus (the expense is 150 g/m\textsuperscript{2}) – 63.2\%, the lowest rates are 39.2\% in the control sample.

Keywords: Biohumus, poultry waste, effective microorganisms, waste bioconversion, microbial utilization, biological product, productivity of wheat, biofertilizer


INTRODUCTION

Recycling of waste and by-products in the branches of food and processing industry provides a number of environmental problems in the sphere of ensuring the sustainable development and protection of the environment [1–3].

Feather-downy waste in the form of by-product is formed in high quantities during commercial poultry processing and, in the chemical relation, is native keratin [2]. The high mechanical stability, hardness and a large number of disulfide bonds of native keratin makes it resistant to the degradation caused by proteolytic enzymes, such as pepsin, trypsin and papain [3, 4, 6]. Due to the high content of nitrogen the accumulation of the formed waste by their storage, burial or burning provides not only the destruction of surface soils, but also considerable losses of biological resources, such as proteins and enzymes [5].

The traditional way of dung removal is burning. However, it is not expedient either from the ecological, or the economic point of view [7]. One of problems of dung utilization by means of burning is a high exit of...
CO₂. Taking into account the pollution caused by the use and change of properties of the used lands, about 9% of evolutions of CO₂ [8] fall to the share of poultry-farming sector in the structure of human activity.

The foremost scientists in the field of ecology have proved that poultry waste burning is pernicious for the planet and mankind. It is stated in a report of the UN that poultry farming is the main source of pollution of water and soil – it provides the formation of more greenhouse gases, than that produced by cars, the intensive poultry farming provides the degradation of soils, the pollution of reservoirs and air [9–11].

The simplest of the existing technologies of utilization of mixtures of feather-downy raw materials and dung is composting. Vast free areas remote from settlements are needed to organize it in the open air. The process lasts from 3 to 6 months and demands periodic turning of heaps for the homogenization of mixture and the activization of activity of microbes [11–15].

The classical technology has been recently supplemented with a lot of modifications. For example, composting with the use of steam-gas plants or enzymatic composting where the speed of process increases several times [16].

In recent years the ways of dung utilization with the use of coprophages (larvae of Musca domestika S., specially grown earthworms Eisenia) have become popular. For example, a unique way of dung processing with the use of house fly larvae has been worked out in the All-Russian Research Institute of Livestock [17, 18]. During the growth of fly larvae the dung mass turns into a slightly damp friable mass with a slight smell [19, 20]. The final product of processing with the use of this way is the fertilizer which is capable to increase considerably the quality and productivity of soil [21–23]. Vermiculture is quite popular in the Western European countries where people have got used to using the line of earthworms Eisenia fetida, or "Red Californian hybrid" [24].

In Russia people use the following hybrids of Red Californian worm: Obinsk, Obolensk, Vladimir and Morevka hybrids [25]. However the method of dung utilization with the use of fly larvae and lines of hybrid earthworms has essential shortcomings: the complexity of maintenance of necessary parameters of temperature and humidity of egg laying and the cultivation of larvae and lines of worms [21–23]; the difficult design of recycling units (the existence of flap doors, a lot of feeders, the complex system of motion of trays along the racks) [26]; the complexity of production organization in the territory of Russia, considering rather low average winter temperatures [27, 28]; the considerable losses of organic substance in the final products: the increased speed of their mineralization and, as a result, the high losses of nitrogen and the formation of a large amount of ammonia [29]; the discrepancy of the final products to the requirements for the physical and chemical composition presented in the Technical specifications of the Russian Federation No. 94991, some international standards and agrochemical indicators [17].

Thus, the technologies of worm composting and the use of fly larvae, even considering all their advantages, are favorable for small farms or for use for one's own needs [25, 28, 29]. The searches of alternative technologies of efficient recycling of waste of the poultry-farming complex have provided the development of biotechnologies, i.e. the use of systems (consortia) of effective microorganisms (EM) capable to process in the course of their activity the organic and inorganic substances, which are part of waste, into efficient final products – fertilizers [8, 31].

In other words, EM provide quick composting – the biological oxidation of organic substrata which provide the enzymatic hydrolysis of keratin – the structural protein of a feather [32].

The activity of effective microorganisms determining the duration and depth of process of biotransformation [32, 33] is the basis of the vast majority of bioconversion technologies. The biological products, biostimulators or the obtained products – biofertilizers (biocomposts) applied in the similar technologies are communities of selected microorganisms, or contain a specific strain of microorganisms of a certain type [17, 33].

The application of biological products for organic waste processing allows to correspond to the latest requirements of production of organic fertilizers of livestock waste [31, 33]. Namely, the preservation of its biological potential, the exclusion of a possibility of presence of pathogenic microorganisms, the elimination of an unpleasant smell and the decrease in the risk of incidence of workers at the enterprises of agrarian and industrial complex [32].

Obtaining biofertilizers on the basis of a chicken feather has drawn attention of research scientists [34] since long ago. Feather meal is cheap and easily available source of nitrogen (15% of N) and can be used as an effective biofertilizer with high biogenous properties.

Biotechnologies are the development and expansion of set of processing methods the roots of which appeared [1] thousands years ago. The application of biotechnologies in agriculture, for example, the application of growth enhancing hydrolyzates of proteins is the perspective trend of development of branch and can effectively be applied in the production of fertilizers [9, 29].

The microbial degradation of feather-downy waste is an alternative to the existing technologies of production of nitrogen fertilizers. There are bacteria capable to use feather-downy waste as the main organic substratum and a source of carbon, nitrogen, sulfur and energy [32, 35]. Indolyl-3-acetic acid is the main growth regulator which increases the availability of nutrients for plants, and also provides the growth of roots [33–36].

The degraded product obtained on the basis of feather waste can become an abundant source of the corresponding amount of tryptophane which is the basis of synthesis of indoleacetic acid [1, 36]. The poultry waste biohumus is the product with a low prime cost and a high efficiency that has a number of advantages in comparison with the existing analogs, in
particular, the pathogenic microflora which is a special problem during efficient waste recycling is completely absent in the biohumus [21, 34, 37, 39].

At the present time, one of the urgent issues is meeting the need of the population for food, and first of all it includes grain and bakery products. Based on this fact, as for efficiency, winter wheat is considered to be potential grain crops. Due to a long vegetative period it is capable to use most fully the solar energy, the nutrients contained in soil and moisture during the autumn and spring period [36–38].

The application of high rates of mineral, in particular, nitrogen fertilizer to receive heavy crops of winter wheat grains when sowing them after the late removed predecessors, which is not always justified from the economic and ecological point of view [2].

Thus, the application of new biological fertilizers is an alternative to the new chemical fertilizers that need to be thoroughly checked [40–44].

OBJECTS AND METHODS OF STUDY

At the previous stage of studies a biological product on the basis of consortium of decomposer microorganisms was developed: Bacillus pumilus AL16, Microbacterium terregens AC1180, Aeromonas sp. B5376, Arthrobacter globiformis AC1529, Streptomyces olivocinereus AC1169 and Acinetobacter sp. B390. The assessment of the compliance obtained with the application of a biological product, biohumus, with the requirements of regulatory documents for fertilizers of livestock and poultry waste, in particular, the sanitary and microbiological and veterinary and sanitary indicators of the obtained biohumus has shown that the optimum time of bioconversion is the term of 14 days. The studies were performed with the substrata with the contents of feather-downy waste and dung of 8 : 2 respectively as this ratio is considered as optimum. As a comparison, samples of raw mixtures of waste were used as the control ones [41].

Field studies of influence of the biohumus obtained from the mixture of poultry wastes on the harvest and quality indicators of winter wheat were performed in 2014–2015 to set the standards of application of biohumus.

The released frost-resistant grades of the winter wheat "Skipetr" and "Zimushka" which steadily provide with heavy crops are chosen as the test crops to assess the efficiency of the developed biohumus.

All the grades of winter wheat impose high requirements for soil properties: high fertility, structure, with the enough content of nutrients, such as nitrogen, phosphorus and potassium. The acidity of soil solution must not exceed the indicator of 7.5, therefore, the medium must be alkalescent or acidic.

Chernozems are considered to be the best soils for winter wheat. They have enormous soil and humus horizons and contain a significant amount of humus (from 8 to 12%).

The agrotechnology standard for the area of studies. The tests were carried out on chernozem soils of the land plots of the Leninsk-Kuznetsky district of the Kemerovo region (Russia). According to the mechanical and agrochemical analyses, this type of chernozem is referred to the soils, heavy in mechanical composition, because of the high content of physical clay (the fraction of 0.01 mm) – up to 72% and bad agrophysical properties – low air and water permeability [39]. The predecessor of crops is the corn prepared as silage.

The studied grades of winter wheat were sown in narrow rows with the sowing rate of 6.0 million of viable seeds per hectare (~ 260 kg/hectare). The experiment was performed on the plots of 50 m². The experiment was made with a triple frequency.

Design of the experiment. Fig. 1 provides the design of experiment of the study of influence of various rates of biohumus on the grades of winter wheat.

Proceeding from the analysis of laboratory results the design of experiment consists of the following stages: the biohumus obtained at the first stage of studies is applied for the plots with a crop of winter wheat with the following rates: 1 – the developed biohumus (the expense is 100 g/m²); 2 – the developed biohumus (the expense is 150 g/m²); 3 – the developed biohumus (the expense is 200 g/m²). The following was used as a comparison: 4 – the organic mineral fertilizer "Universal'noe" (the expense according to the instruction is 150 g/m²); 5 – the control (without the application of biohumus). Determination of protein and protein fractions in grains. The protein in the grain obtained according to the design of the experiment was determined in accordance with GOST 10846-91 "Grain and products of its processing. Method for determination of protein" with the use of Kjeldahl flask. The protein fractions of grain were determined using the method of gel penetrating planar chromatography (GPPC).

Fig. 1. Design of the experiment.
RESULTS AND DISCUSSION

Table 1 provides the results of a study of determination of the optimum norm of application of the developed biohumus for winter wheat of the grades "Skipetr" and "Zimushka".

According to the data presented in Table 1, the application of the organic mineral fertilizer “Universal'noe” (the expense is 150 g/m²) and the use of the developed biohumus (the expense is 150 g/m²) provided an increase in its growth, compared with the control sample of the wheat “Skipetr”, by 12 and 15 cm (the stem elongation stage), by 15 and 18 cm (the earing stage), by 21 and 30 cm (the milk stage) and by 19 and 30 cm (the firm ripe stage) respectively.

The use of these biohumus variants has provided the best indicators, both for the grade “Skipetr”, and for the wheat of the grade “Zimushka”. The above values for the grade “Zimushka” were within the similar limits: an increase in its growth, compared with the control sample, by 17 and 18 cm (the stem elongation stage), by 19 and 21 cm (the earing stage) and by 19 and 31 cm (the milk stage and the firm ripe stage) respectively.

The results provided in the experiment in the study and analysis of dynamics of accumulation of dry weight when applying the developed biohumus and the organic mineral fertilizer “Universal'noe” were unequal. Thus, at the stem elongation stage the largest amount of dry weight is noted in the samples with the application of the organic mineral fertilizer “Universal'noe” (the expense is 150 g/m²) and with the use of the developed biohumus (the expense is 150 g/m²). The maximum gain at the earing stage was noted in the sample with the application of the developed biohumus (the expense is 150 g/m²), and was 340 g per 100 plants (the grade “Zimushka”).

The dry biomass in the control sample (without the use of biohumus) and in the variant with the application of the developed biohumus (the expense is 200 g/m²) is nearly 1.5–2.0 times lower than that in the variant with the application of the developed biohumus (the expense is 150 g/m²). This regularity in the dynamics of dry biomass is characteristic of the milk stage and the firm ripe stage.

The maximum gain in the noted phases is also in the variants with the application of the developed biohumus (the expense is 150 g/m²) and the organic mineral fertilizer “Universal'noe”.

It is known that the volumes of future harvest are characterized by two basic indicators – the density of productive plant stand and the mass of grain of one ear. These components are the generalizing characteristics of a harvest of winter wheat grains of any grade. Table 2 presents the results of calculation of the above-mentioned indicators during the application of biohumus.

Table 1. Dynamics of the growth (cm) and the accumulation of dry biomass (g/100 sol.) of winter wheat of the grades “Skipetr” and “Zimushka” in the plants depending on the rates of the applied biohumus or fertilizers (the average for 2014–2015)

<table>
<thead>
<tr>
<th>Variant of experiment</th>
<th>Growth dynamics (cm) / dry biomass accumulation (g/100 sol.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stem elongation stage</td>
</tr>
<tr>
<td>“Skipetr”</td>
<td>75/143</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 100 kg/m²)</td>
<td>75/143</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 150 g/m²)</td>
<td>88/155</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 200 g/m²)</td>
<td>87/133</td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal'noe”</td>
<td>85/133</td>
</tr>
<tr>
<td>(the expense is 150 g/m²)</td>
<td>85/133</td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>73/80</td>
</tr>
<tr>
<td>“Zimushka”</td>
<td>79/143</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 100 kg/m²)</td>
<td>79/143</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 150 g/m²)</td>
<td>92/157</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 200 g/m²)</td>
<td>90/136</td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal'noe”</td>
<td>91/137</td>
</tr>
<tr>
<td>(the expense is 150 g/m²)</td>
<td>91/137</td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>74/83</td>
</tr>
</tbody>
</table>
Table 2. Influence of various rates of biohumus on the indicators of structure of a harvest of winter wheat of the grades “Skipetr” and “Zimushka” (the average for 2014–2015)

<table>
<thead>
<tr>
<th>Variant of experiment</th>
<th>Tilling capacity</th>
<th>Ear length, cm</th>
<th>Quantity of cones per ear, pcs</th>
<th>Quantity of grains per ear, pcs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total</td>
<td>productive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Skipetr”</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus (the expense is 100 kg/m²)</td>
<td>486.0</td>
<td>300.0</td>
<td>5.6</td>
<td>11.0</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 150 g/m²)</td>
<td>566.0</td>
<td>307.0</td>
<td>6.2</td>
<td>13.5</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 200 g/m²)</td>
<td>474.0</td>
<td>266.0</td>
<td>5.0</td>
<td>10.5</td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal’noe” (the expense is 150 g/m²)</td>
<td>562.0</td>
<td>303.0</td>
<td>6.1</td>
<td>13.8</td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>332.0</td>
<td>280.0</td>
<td>4.6</td>
<td>10.1</td>
</tr>
<tr>
<td>“Zimushka”</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus (the expense is 100 kg/m²)</td>
<td>493.0</td>
<td>305.0</td>
<td>5.9</td>
<td>12.0</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 150 g/m²)</td>
<td>575.0</td>
<td>312.0</td>
<td>6.6</td>
<td>14.0</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 200 g/m²)</td>
<td>555.0</td>
<td>299.0</td>
<td>6.1</td>
<td>13.7</td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal’noe” (the expense is 150 g/m²)</td>
<td>570.0</td>
<td>308.0</td>
<td>6.5</td>
<td>14.0</td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>337.0</td>
<td>284.0</td>
<td>4.9</td>
<td>10.6</td>
</tr>
</tbody>
</table>

The highest tilling capacity is shown in the variants of experiments with the application of the developed biohumus (the rate is 150 g/m²) of the grade “Skipetr” (the total is 566.0 pieces/m, the productive capacity is 307.0 pieces/m); of the grade “Zimushka” (575.0 and 312.0 pieces/m respectively) and of the organic mineral fertilizer “Universal’noe” (the expense is 150 g/m²), of the grade “Skipetr” (the total is 562.0 pieces/m, the productive capacity is 303.0 pieces/m) and of the grade “Zimushka” (570.0 and 308.0 pieces/m respectively).

Thus, proceeding from the data presented in Tables 1 and 2 it is possible to draw a conclusion that biohumus has a positive effect on the indicators of harvest of the grades of winter wheat “Skipetr” and “Zimushka” under conditions of the Kemerovo region.

Fig. 2 presents the photo of result of use of biohumus for a crop of winter wheat of the grade “Skipetr” in comparison with the control sample (without the use of fertilizers).

As a result of the studies it has been established that the developed biohumus with the application rate of 150 g/m² has the highest positive effect.

The application of biohumus allows to increase the quality indicators of composition of a wheat harvest (Table 3).

![Fig. 2. Photo of wheat of the grade “Skipetr”: (a) Control (without processing); (b) Processing using biohumus with the rate of 150 g/m².](image-url)
Table 3. Change of productivity and quality indicators of winter wheat grains caused by the use of biohumus, t/hectare (the average for 2014–2015)

<table>
<thead>
<tr>
<th>Variant of experiment</th>
<th>Productivity, t/hectare</th>
<th>Increase, t/hectare</th>
<th>Thousand grain weight, g</th>
<th>Grain unit, g/l</th>
<th>Protein, %</th>
<th>Starch, %</th>
<th>Ash, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Skipetr”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus</td>
<td>4.15</td>
<td>0.89</td>
<td>40.00</td>
<td>770.00</td>
<td>14.15</td>
<td>68.54</td>
<td>1.70</td>
</tr>
<tr>
<td>(the expense is 100 kg/m²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus</td>
<td>4.63</td>
<td>1.25</td>
<td>44.00</td>
<td>783.00</td>
<td>15.02</td>
<td>67.00</td>
<td>1.63</td>
</tr>
<tr>
<td>(the expense is 150 g/m²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus</td>
<td>4.13</td>
<td>0.92</td>
<td>41.00</td>
<td>772.06</td>
<td>14.25</td>
<td>63.34</td>
<td>1.54</td>
</tr>
<tr>
<td>(the expense is 200 g/m²)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal’noe”</td>
<td>4.23</td>
<td>1.12</td>
<td>44.00</td>
<td>783.00</td>
<td>14.76</td>
<td>68.55</td>
<td>1.73</td>
</tr>
<tr>
<td>(the expense is 150 g/m²)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>3.18</td>
<td>–</td>
<td>39.00</td>
<td>758.00</td>
<td>13.20</td>
<td>63.70</td>
<td>1.94</td>
</tr>
<tr>
<td>“Zimushka”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus</td>
<td>4.33</td>
<td>1.05</td>
<td>42.00</td>
<td>784.00</td>
<td>14.56</td>
<td>70.70</td>
<td>1.90</td>
</tr>
<tr>
<td>(the expense is 100 kg/m²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus</td>
<td>4.42</td>
<td>1.15</td>
<td>45.00</td>
<td>789.00</td>
<td>15.10</td>
<td>71.54</td>
<td>1.62</td>
</tr>
<tr>
<td>(the expense is 150 g/m²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus</td>
<td>4.13</td>
<td>1.13</td>
<td>43.00</td>
<td>786.00</td>
<td>14.58</td>
<td>70.79</td>
<td>1.70</td>
</tr>
<tr>
<td>(the expense is 200 g/m²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal’noe”</td>
<td>4.53</td>
<td>1.11</td>
<td>44.00</td>
<td>787.00</td>
<td>15.00</td>
<td>69.03</td>
<td>1.69</td>
</tr>
<tr>
<td>(the expense is 150 g/m²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>3.17</td>
<td>–</td>
<td>41.00</td>
<td>769.00</td>
<td>14.32</td>
<td>66.64</td>
<td>2.01</td>
</tr>
</tbody>
</table>

The positive effect on the indicator of productivity depending on the use of biohumus, as for the grade “Skipetr”, was 0.89, 1.25, 0.92 and 1.12 t/hectare relating to the control samples, and 1.05, 1.15, 1.13 and 1.11 t/hectare for the grade “Zimushka”.

The high weight of 1000 grains characterizes one of the main components of high productivity of wheat winter grains.

A significant amount of authors studied the dependence of productivity and quality indicators of winter wheat grains on the weight of 1000 grains [43–46]. The analysis of results of studies in these works shows that the weight of 1000 grains of the grades of winter wheat studied by the authors changes depending on the features of the grade, the conditions of cultivation of winter wheat seeds and the climatic and weather characteristics of the area.

The studied variants of biohumus with various application rates considerably differ concerning this indicator – the difference in the weight of 1000 grains is on average 5 g. The highest weight of 1000 wheat grains was in the experiment variant where the developed biohumus with the application rate of 150 g/m² – 44 g and the organic mineral fertilizer “Universal’noe” (the expense is 150 g/m²) – 44 g, as well, for the grade “Skipetr” and 45 and 44 g for the grade “Zimushka”, respectively, were used.

Confirming the data submitted in the studies [42–47], we draw a conclusion that the change of weight of 1000 grains depending on experiment variants is characterized by the biological features of a grade of winter wheat and the environmental conditions, however the relative fineness of grain remains.

In the experiments the grain variants obtained with the application of biohumus had an unequal unit the indicator of which fluctuated within 758–783 g/l for the grade “Skipetr” and a high grain unit was noted in the grade “Zimushka” – within 769–789 g/l. On average, the experiment variants with the application of the developed biohumus with the rate of 150 g/m² and the organic mineral fertilizer “Universal’noe” (the expense is 150 g/m²) have the highest indicators of unit for the grade “Skipetr” and “Zimushka”. Thus, as a result of the studies a considerable positive influence of the developed biohumus on the productivity of wheat grades “Skipetr” and “Zimushka” with the application rate of 150 g/m² has been established.

Table 4 presents the results of determination of protein in the grains of the grades “Skipetr” and “Zimushka” depending on the rates of the applied biohumus. According to the data presented in Table 4 the application of all rates of the developed biohumus and also the use of the organic mineral fertilizer “Universal’noe” for the crop of winter wheat provides an increase in biosynthesis processes and consequently the growth of percentage of protein in grains.
Table 4. Change of protein content in winter wheat grains caused by the use of biohumus, % (over a period of 2014–2015)

<table>
<thead>
<tr>
<th>Variant</th>
<th>Years of studies</th>
<th>Years of studies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2014</td>
<td>2015</td>
</tr>
<tr>
<td>“Skipetr”</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus (the expense is 100 kg/m²)</td>
<td>10.95</td>
<td>12.84</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 150 g/m²)</td>
<td>11.77</td>
<td>14.25</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 200 g/m²)</td>
<td>11.52</td>
<td>12.37</td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal'noe” (the expense is 150 g/m²)</td>
<td>11.52</td>
<td>11.91</td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>10.78</td>
<td>10.86</td>
</tr>
<tr>
<td>“Zimushka”</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus (the expense is 100 kg/m²)</td>
<td>11.52</td>
<td>12.37</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 150 g/m²)</td>
<td>10.39</td>
<td>28.45</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 200 g/m²)</td>
<td>10.19</td>
<td>28.41</td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal'noe” (the expense is 150 g/m²)</td>
<td>9.98</td>
<td>29.29</td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>9.63</td>
<td>27.64</td>
</tr>
</tbody>
</table>

On average, the percent of protein in the grains of the grade “Skipetr” with the application of the developed biohumus increased by 1.87%, and by 1.11% for the grade “Zimushka” over a period of 2014 and 2015. The use of the organic mineral fertilizer “Universal'noe” has provided an increase in protein by 0.39 and 1.36% respectively.

Presumably, the application of biohumus accelerates the exchange of nitrogenous substances, thus, starting the process of nitrogen reduction.

According to the results of the studies of protein fractions of winter wheat grains, the use of the developed biohumus for the grades “Skipetr” and “Zimushka” changes the ratio of protein fractions. The data are presented in Table 5.

Table 5. Change of fractional composition of protein of winter wheat grains depending on the rates of the applied fertilizers, mg/kg (the average for 2014–2015)

<table>
<thead>
<tr>
<th>Variant</th>
<th>Albumins</th>
<th>Globulins</th>
<th>Prolamins</th>
<th>Glutelins</th>
<th>Total protein</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Skipetr”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus (the expense is 100 kg/m²)</td>
<td>9.17</td>
<td>26.53</td>
<td>54.12</td>
<td>33.91</td>
<td>123.73</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 150 g/m²)</td>
<td>9.85</td>
<td>27.12</td>
<td>55.99</td>
<td>34.90</td>
<td>127.86</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 200 g/m²)</td>
<td>9.12</td>
<td>26.17</td>
<td>53.56</td>
<td>33.69</td>
<td>122.51</td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal'noe” (the expense is 150 g/m²)</td>
<td>9.54</td>
<td>27.04</td>
<td>54.89</td>
<td>33.72</td>
<td>125.19</td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>8.83</td>
<td>26.17</td>
<td>52.65</td>
<td>32.64</td>
<td>120.29</td>
</tr>
<tr>
<td>“Zimushka”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developed biohumus (the expense is 100 kg/m²)</td>
<td>9.78</td>
<td>29.13</td>
<td>54.09</td>
<td>33.01</td>
<td>126.01</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 150 g/m²)</td>
<td>10.39</td>
<td>28.45</td>
<td>57.79</td>
<td>38.13</td>
<td>134.76</td>
</tr>
<tr>
<td>Developed biohumus (the expense is 200 g/m²)</td>
<td>10.19</td>
<td>28.41</td>
<td>57.61</td>
<td>36.89</td>
<td>133.10</td>
</tr>
<tr>
<td>Organic mineral fertilizer “Universal'noe” (the expense is 150 g/m²)</td>
<td>9.98</td>
<td>29.29</td>
<td>54.59</td>
<td>35.23</td>
<td>129.09</td>
</tr>
<tr>
<td>Control (without the application of biohumus)</td>
<td>9.63</td>
<td>27.64</td>
<td>53.89</td>
<td>33.55</td>
<td>124.71</td>
</tr>
</tbody>
</table>

In winter wheat grains of the grade "Skipetr" there is an increase in protein fractions under the influence of medicines: albumines – by 0.2–1.5 mg/g. The similar concerned the other fractions as well. The prolamine fraction in the variant with the use of the developed biohumus with the application rate of 150 g/m² exceeds the control sample by 3.34 mg/g relating to the grade "Skipetr", and by 3.90 mg/g relating to the grade "Zimushka". In general, the results of the studies of change of fractional composition of grain proteins testify that the application of biohumus provides an increase in gluten fractions.

The work provides the assessment of production expenses of cultivation of wheat grades (using an example of the grade "Skipetr") depending on the rate of application of biohumus (Table 6).
The analysis of economic efficiency has shown that the largest investments are required during the cultivation of wheat with use of the organic and mineral fertilizer "Universal'noe" – 32600 rub/ha and the smallest in the variant without the application of biohumus or any other fertilizers – the control variant – 21790 rub/ha. However, in view of various productivity of grains of wheat which changes depending on the influence of various rates of biohumus, the product unit cost considerably changes and is within the limits of 423.8 (biohumus, the expense is 150 g/m²) – 510.3 rub/centner (control). The variant with the use of the developed biohumus (the expense is 150 g/m²) has the highest level of profitability – 63.2%, the control sample has the smallest level – 39.2%.

Thus, at the level of profitability of 63.2% it is necessary to grow up winter wheat of the grade "Skipet" with the use of biohumus with the application rate of 150 g/m² on chernozem soils of the land plots of the Kemerovo region for receiving heavy grain crops (4.4–4.7 t/ha) with high quality indicators.

ACKNOWLEDGEMENTS

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REFERENCES


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ANTIBACTERIAL EFFECT OF COLLOIDAL SOLUTIONS OF SILVER NANOPARTICLES ON MICROORGANISMS OF CEREAL CROPS

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Abstract: Due to the growing problem of decrease in the quality and biological safety of food raw materials and the food obtained from it, the increase in the measures for grain improvement as one of the main vegetable resources of food productions is a necessary condition in the modern food industry. A perspectively new way of providing biosafety of grain raw materials is the use of silver nanoparticles. The present work provides data on the inhibiting influence of silver colloidal solutions on the bacterial composition of microflora of the most demanded grain crops of wheat and rye. Various antimicrobial efficiency of influence of the chosen colloidal solutions "Adzhenta colloidal silver" and "Colloidal silver concentrate KND-S-K" within 24 and 144 hours after the processing of grain crops has been shown. Various influence of experimentally chosen concentrations of solutions of silver nanoparticles of 0.1 g/dm\textsuperscript{3} and 0.075 g/dm\textsuperscript{3} on the number of viable cells of grain bacteria has been described. An approximate mechanism of effect of colloidal solutions of silver nanoparticles on the bacterial cells of microorganisms has been stated. A negative role of bacterium \textit{Bacillus subtilis} in grain production has specially been noted. Their identification in grain crops has been performed and measures for effective destruction of them in grain by means of silver nanoparticles have been proposed. The current data can be used for providing biosafety of grain and an effective solution of the problems on its processing for the purpose of manufacturing of quality products.

Keywords: Silver nanoparticles; food production; grain biosafety; \textit{Bacillus subtilis}

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INTRODUCTION

Nanodimensional structures of silver metals are a perspectively new type of materials used in scientific research due to their versatile application in various areas [1, 2].

In comparison with other metals, silver has strongly marked bactericidal and fungicide characteristics. Besides, the use of silver in the form of nanoparticles has allowed to manipulate its size and properties at the nanolevel which resulted in an increase in the antimicrobial potential. As with a decrease in the size of particles the specific phase interface increases and the area of contact of silver with bacteria considerably extends. Thus, it is confirmed that the bactericidal effect of silver nanoparticles depends on their sizes. And even after long processing, the ability of microorganisms to develop resistance to nanoisilver [3] hasn’t been observed.

The value of silver nanoparticles (SNP) in the food industry – the technologies of application of colloidal systems in the following developments – should specially be noted:

- the manufacturing of packing materials covered with a nanofilm with bactericidal and fungicide properties;
- the use of biodegradable nanosensors to control the temperature and humidity of foodstuffs;
- the addition of emulsion nanosystems in food to increase nutrient availability;
- the development of chelate nanocompounds for more effective delivery of nutrients to cells without a change of color and taste of food;
- receiving nanodisperse amplifiers of taste and aroma;
- the production of nanodimensional powders that make it easier to digest nutrients;
- the use of the nanoparticles capable to take up and remove selectively food contaminants, for example, mycotoxins;
- the development of the antimicrobial nanocomponents providing control for the development of infectious agents of food infections;
- the creation of nanosensors for the identification of vegetable and animal pathogens;

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the use of fluorescent nanoparticles with attached antibodies for the determination of chemicals or food pathogens [4, 5, 6].

Studies in the scope of SNP as an antimicrobial agent when developing antibacterial means against a number of bacteria and filamentous fungi are of great interest in the food industry [7, 8].

It is due, first of all, to the growing problem of a decrease in the quality and biological safety of foodstuffs at all stages of production and storage as a result of high adaptive ability of pathogenic microorganisms to the changing conditions of the environment [9, 10].

Special vigilance is caused, in particular, by practical lack of application of effective and eco-friendly measures for the improvement of grain production. Grain is provided quite well with the nutrients which are a favorable environment for the development of microorganisms under certain conditions. The significant amount of microorganisms negatively influence grain under certain favorable conditions, in other words, they reduce the content of solids in it, provide its pollution, and also poison it with toxic waste products. The contamination of grain by depredators and diseases is revealed during its further processing in the food industry. In this regard, the negative processes in the flour-grinding and baking industries are a serious threat to human health, provide a further decrease in the quality of bakery products. The contamination of grain by infectious agents of the mushroom and bacterial etiology occurs annually to some extent and though the level of contamination is corrected by a number of edaphoclimatic and anthropogenous factors, the harvest shortage can make in some cases up to 30% with a simultaneous decrease in the technological and baking qualities of grain [10, 11].

An important role in the decrease in the harvest and quality indicators of grain and its derivative products, in particular bread, is played by the infectious agents of bacterioses – sporous bacteria of Bacillus mesentericus vulgaris Flügge and Bacillus subtilis and other species of this genus [12, 13].

According to the most widespread systematics of phytopathogenic bacteria [14] based on the signs of existence or lack of flagella, Gram staining of colonies and their pigmentation, the genus Bacillus which is a part of the Bacillaceae family is presented by the most harmful types.

After cooling of bread, in case of low acidity and the temperature above 25°C, the sporous forms of infectious agent begin to develop causing chemical changes in the newly-baked bread. Under the influence of the active amylases emitted by the bacteria in bread the quantity of dextrines which provide the mucilagination of the crumb, loss of its structure and the formation of emptiness increases. Under the influence of proteolytic enzymes of bacteria disintegration products of proteins that give a pungent specific smell to bread are formed. Such bread is not suitable for consumption, nor as animal forage either.

A different degree of contamination by bacteria spores is noted on wheat and corn grain, in soft and hard wheat flour, in bran and other products which are raw materials for bread and bakery products [15, 16, 17].

All the above allows to establish the fact of a huge damage sporous bacteria and other phytopathogenic microorganisms may cause to the food market of the country. The infectious agents of bacterial etiology are wide-spread and have a high level of injuriousness which, along with the decrease in productivity, consists of the contamination of wheat grain providing loss of technological and baking properties in the latter.

Due to this, the main purpose of this work is the study of influence of various concentrations containing silver nanoparticles on the viability of bacterial microbiota of seeds of some grain crops.

OBJECTS AND METHODS OF STUDY

To study the contamination of grain crops, seeds of Irgin summer wheat (Triticum aestivum L.) and Krone winter rye (Secale cereale) were used as the objects. The quantitative and qualitative composition of bacterial microflora of grain was studied using the method of electronic microscopy.

To inhibit the processes of microbiological spoilage of grain crops the SNP colloidal solutions "Adzhenta colloidal silver" (the manufacturer is LLC "KorolevFarn", Russia) and the colloidal solution of silver nanoparticles KND-S-K (Scientific and Production Enterprise LLC "Sentoza Faktoring NP", Russia) were used.

Using the method of dynamic laser light scattering dispersion and distribution was studied by the sizes of nanoparticles in the studied colloidal solutions. The test specimens with the volume of 0.7–3.0 ml were placed in the ditch of the device and measurements were taken at a temperature of 23 ± 1°C using the laser particle size analyzer Nanotrac – the modification of Zetatrac ("Microtrac Inc.", the USA) – by means of the Microtrac FLEX software.

The studied SNP colloidal solutions, using the method of dilution by distilled water, brought up to the use rates of 0.075 and 0.1 g/dm³ which had experimentally been selected taking into account the compliance to normative documents in the tolerant (transferable) content of silver in drinking water (WHO, SanPiN) [18, 19]. Seeds of wheat and rye were processed using the obtained solutions. For this purpose 50 g of seeds and the calculated dose of preparative form of silver colloidal solution taking into account the concentrations of nanoparticles were put into a 150 ml flask. The flask with seeds was stirred up for 2–3 minutes before the full distribution of the preparation on the surface of seeds. Then the processed grain was left for 2 hours after which the test specimens of the studied samples were selected and put into sterile ware in the aseptic conditions excluding the microbial contamination of raw materials and total of bacteria using the method of washed out crops with the dilution degree of 1 : 100 per meat-and-peptone agar (MPA) with the subsequent cultivation at the temperature of 30 ± 1°C for 24–48 hours was determined.

101
To study the influence of SNP on the bacterial microbiota of grain crops in detail the analysis of contamination of samples was also performed in 24 and 144 hours after processing. The choice of temporary intervals is justified, among other things, by the features of development of microflora of grain crops (by the antagonistic effect of some microorganisms on others).

To study the qualitative composition of microflora, microscopic preparations (fixed dabs painted according to Gram - to study bacterial morphology) were made of the colonies of the microorganisms differing from each other in cultural properties.

The spore-forming bacteria of the genus *Bacillus* were determined using the technique described in GOST ISO 21871 [20]. Initially, inoculation, first, of a liquid enriched medium (tryptone soy polymixil broth (TSPB) with the established volume of initial sample of suspension of 10 ml in the pasteurized washouts from the samples at the rate of 1 : 100 was consistently performed. The duration of incubation was 48 h at a temperature of 30°C. Then, a transfer to a solid nutrient medium (PEMBA) and incubation for 18–48 h at 37°C for the further analysis of Petri dishes to check the presence of the colonies which, according to the characteristics, can correspond to presumptive *Bacillus* bacteria was performed. Microbiological medium from HiMedia Laboratoris, India, Merck Ltd., SRL Pvt., Ltd., Mumbai were used to perform the studies.

**RESULTS AND DISCUSSION**

According to TR TS 021/2011 certain complexes of microorganisms of grain crops (Table 1) [21] are normalized.

The determination of content of microorganisms of the studied grain has shown compliance with the normalized indicators, except the indicator of the total plate count. According to the obtained data, the indicator was $9.0 \times 10^3$ CFU/g and $7.0 \times 10^3$ CFU/g for wheat and rye respectively with the norm of $5.0 \times 10^3$ CFU/g.

When studying the qualitative composition of microbiota of wheat and rye seeds it has been established that the bacterial complex is presented by: Gram-negative bacteria *Erwinia herbicola*, *Escherichia coli* and *Pseudomonas fluorescens* and Gram-positive spore-forming bacteria of the genus *Bacillus* (presumably *Bacillus subtilis*), *Clostridium perfringens* and gram-positive cocci.

The results of the experiments according to the method [20] of identification of bacteria of the genus *Bacillus* in the composition of microfloras of grain crops show the existence of this type of microorganisms in wheat seeds and the absence of them in rye seeds (Fig. 1). True to form, the colonies that correspond to the representatives of bacteria of the genus *Bacillus* (Fig. 1a) have sizes from 2 mm to 5 mm, uneven edges with branchings on a smooth glass surface, a whitish-gray color in the center and a blue/turquoise background, and also a deposit aureole (the egg yolk reaction) up to 5 mm wide.

**Table 1. Microbiological standards of grain safety**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Norm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total plate count, CFU/g, not more than</td>
<td>$5.0 \times 10^3$</td>
</tr>
<tr>
<td>Escherichia coli group bacteria, not permitted in the mass of the product (g)</td>
<td>0.01</td>
</tr>
<tr>
<td>Mold, CFU/g, not more than</td>
<td>50.0</td>
</tr>
<tr>
<td><em>B. cereus</em>, not permitted in the mass of the product (g)</td>
<td>0.1</td>
</tr>
<tr>
<td>Pathogenic microorganisms, including salmonellas, are not permitted in the mass of the product (g)</td>
<td>25.0</td>
</tr>
</tbody>
</table>

![Fig. 1. Visual analysis of presumptive bacteria of the genus *Bacillus* of microflora: (a) of wheat seeds, (b) of rye seeds.](image)
Lack of the colonies that correspond to bacteria of the genus *Bacillus* bacteria in the analysis of bacterial microbiota of rye seeds (Fig. 1b) is explained probably by various susceptibility of plants to this complex of microorganisms, and also by the factors of the external environment of cultivation of seeds [22, 23, 24]. Besides, the rye grain taken for the study differed initially from wheat grains by lower contamination by microorganisms as a result of the initial analysis of content of microorganisms.

As for cultural and morphological features, it is possible to draw a conclusion that this kind of bacterium belongs to *Bacillus subtilis*. This culture forms flat, dry colonies of dense consistency with a specifically white granular deposit that can easily be taken off from the agar. The diameter is 2.5 mm. The edges are almost straight or slightly rugged. Other types of colonies have not been noted.

To confirm the colonies that correspond to representatives of bacteria of the genus *Bacillus subtilis* it has been also established using the microscopy method that the bacteria allocated by us from the microbiota of wheat seeds correspond to this kind. These are Gram-positive thin sticks of 3–5×0.9 microns, they are separate and have the form of threads or chains. They may contain ellipsoidal or cylindrical spores the diameter of which is not higher than the width of a microbic cage (Fig. 2).

On the basis of the obtained data on the quantitative and qualitative composition of microorganisms of the studied grain crops a need of their processing by antimicrobial means to prevent a microbiological damage has been determined.

The establishment of antibacterial activity of SNP solutions depending on the concentration and duration of processing of grain crops was the following stage of work, the obtained data are presented in Table 2.

Proceeding from the basic data on the content of the total viable count in raw grain crops it is possible to note that the least antibacterial effect of SNP can be observed after 2 hours of processing of grain of wheat and rye regardless of the concentrations and the type of colloidal solutions. At the same time, it is known from the studies performed earlier that the access of SNP to the cellular wall is complicated with a high concentration of bacterial cells, and a smaller amount of particles is adsorbed on its surface which provides a decrease in the biocidal effect [25].

It was shown during the subsequent quantitative analysis of bacterial microflora of grain that after 24 hours of processing the colloidal solutions of nanoparticles with the concentration of 0.1 g/dm³, in general, show a deeper effect against the complex of microorganisms of grain crops in comparison with the lower concentration of SNP of 0.075 g/dm³.

At the same time it should be noted that the control of the samples of grain processed by SNP after 24 hours has shown almost full compliance with the norms of TR TS 021/2011 [21]. Thus, it is obvious that SNP colloidal solutions are capable to inhibit effectively the development of bacterial microbiota of grain crops.

Analyzing the quantity of microorganisms in the grain processed after 144 hours it is possible to come to a conclusion that the influence of SNP is already insignificant in comparison with the previous period of processing (2–24 h).

At the same time, estimating the antimicrobial effect of colloidal solutions of the chosen concentrations after 144 hours by comparison of their inhibiting influence on microorganisms, it is fair to note that SNP solutions with the concentration both of 0.075 g/dm³ and 0.1 g/dm³ have the highest effect in both chosen preparations.

The obtained data have also been presented in the form of diagrams (Fig. 3 a–d).

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**Table 2. Antimicrobial activity of various concentrations of colloidal solutions of nanoparticles**

<table>
<thead>
<tr>
<th>Cultivation time</th>
<th>Total viable microorganisms in wheat, (CFU/g)</th>
<th>Total viable microorganisms in rye, (CFU/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adzhenta</td>
<td>KND-S-K</td>
</tr>
<tr>
<td>0.1 g/dm³</td>
<td>0.075 g/dm³</td>
<td>0.1 g/dm³</td>
</tr>
<tr>
<td>2 h</td>
<td>8·10⁴</td>
<td>7·10³</td>
</tr>
<tr>
<td>24 h</td>
<td>5·10⁴</td>
<td>5·10³</td>
</tr>
<tr>
<td>144 h</td>
<td>4·10⁴</td>
<td>3·10³</td>
</tr>
</tbody>
</table>

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**Fig. 2. Microscopic analysis of bacteria of the genus *Bacillus subtilis***.
At the same time, it is necessary, based on the performed studies, to emphasize quite a high antimicrobial influence of Adzhenta colloidal silver after 24 hours of processing in all the samples of grain in comparison with the solution of silver nanoparticles KND-S-K. Most likely, various ways of obtaining and stabilizing SNP in the solution of the used preparations are the reason for that. It is well known that atoms of metals have a high chemical activity which remains in the clusters and nanoparticles, which are formed of atoms, with a large number of atoms which can provide a sharp decrease in their activity [26, 27].

The SNP solutions of colloidal degree of dispersion of KND-S-K stabilized by arabic gum, chitosan and sulfoamber acid with the particles of 6–20 nanometers (Fig. 4) have a high antimicrobial effect, but in many respects depend on the physical and chemical factors of the environment due to the chemical method of stabilization [28, 29]. Chemically, Adzhenta colloidal silver is silver nitrate and is produced without any chemical processes, with the use of an electromagnetic charge which suspends silver particles of 5–15 nanometers (Fig. 5) in water with the formation of solution. Therefore, most likely it shows a more considerable effect.

Besides, as it is reported from the literary data [26, 30], the mechanism of inhibition of SNP is directly related to their size (less than 100 nanometers) and the largest surface area to volume. It is known that with a decrease in the size of particles the specific phase interface and, therefore, the comparative concentration of active silver increases which provides an increase in the area of contact of silver with bacteria.

At the stage of study of influence of SNP colloidal solutions on the presence of a bacterium of the genus *Bacillus subtilis* in the processed wheat sample, the results of the performed study also specify that under the influence of SNP there is destruction of a bacterial cell after 24 hours of cultivation in both chosen preparations. The effect of colloidal solutions was already shown in both cases with the concentration of 0.075 g/dm³.

Fig. 3. Diagram of antibacterial activity of silver nanoparticles of various preparations on microorganisms: (a) of wheat with the concentration of 0.1 g/dm³; (b) of wheat with the concentration of 0.075 g/dm³; (c) of rye with the concentration of 0.1 g/dm³; (d) of rye with the concentration of 0.075 g/dm³.
Fig. 4. Histogram of distribution of nanoparticles by size in the KND-S-K colloidal solution.

Fig. 5. Histogram of distribution of nanoparticles by size in the Adzhenta colloidal solution.

Thus, based on the results of the performed studies, it is possible to draw a conclusion that the addition of the preparation "Adzhenta colloidal silver" into the grain mass with the concentration of SNP of 0.1 g/dm³ will allow after 24 hours to prevent the development of microbial contamination, will increase the period of storage and the quality of grain, and also provide the inhibition of further development of spore-forming forms of bacteria of the genus *Bacillus subtilis*. The processing of grain mass using the solution of silver nanoparticles KND-S-K of 0.1 g/dm³ within 24 hours will also favorably effect the inhibition of bacterial microbiota of grain crops.

CONCLUSION

The performed study was developed to show the efficiency of antibacterial preparations of a new generation – nanodimensional silver dispersions for the food industry.

As a result of the done work, a method of application of preparations of silver nanoparticles to reduce the microbial contamination in the grain processing and baking industry providing an increase in the microbiological purity of grain for the purpose of providing biological safety has been offered.

Antibacterial properties of nanoparticles of Adzhenta colloidal silver and KND-S-K on the basis of understanding of their effect to prove their efficiency against various pathogenic microorganisms of grain crops have been studied.

Various results of effect of SNP preparations of the colloidal degree of dispersion (KND-S-K, Adzhenta) depending on the concentrations in the solution have been obtained and the preferable modes of processing of grain crops have been chosen. On the basis of results of the studies biostatic concentrations of SNP preparations have been determined.

The efficiency of their application against significant pathogenic bacterial microorganisms of grain productions has been proved (in particular, against *Bacillus subtilis*).

It has been established on the basis of study of influence of SNP colloidal solutions on the bacterial microbiota of grain of wheat and rye that SNP are capable to inhibit effectively the activity of the bacterial microorganisms that contaminate grain raw materials.

Finally, the conclusions provided in this work will help us to apply SNP colloidal solutions to inhibit the growth of bacterial microorganisms and reduce considerably the level of microbiological contamination of grain crops.

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DETERMINATION OF THE INTENSITY OF BACTERIOCIN PRODUCTION BY STRAINS OF LACTIC ACID BACTERIA AND THEIR EFFECTIVENESS


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Abstract: The study of bacteriocins is one of the most relevant areas of research. This is due to the increase in the number of pathogenic microorganisms resistant to antibiotics. The bacteriocins of lactic acid bacteria have the most common application because of their safety in use. To assess the antimicrobial potential of bacteriocins of lactic acid bacteria and the possibilities for their further use, this study deals with the intensity of bacteriocin production by strains of lactic acid bacteria, the minimal inhibitory concentration of bacteriocins produced by these strains with respect to E. coli B-6954, as well as the antimicrobial activity of the produced bacteriocins with respect to some strains of pathogenic microorganisms. This work was carried out on the basis of the Kemerovo Technological Institute of Food Industry (Russia). The study objects were strains of microorganisms Lactobacillus delbrueckii B2455, Lactobacillus paracasei B2430, Lactobacillus plantarum B884. Biomass concentration was determined by spectrophotometric method. Study of antimicrobial activity in relation to a number of pathogenic strains was carried out in a culture fluid by optical density, and also by a disk-diffusion test. As a result, the maximum productivity value, characterizing the intensity of bacteriocin production, was observed for strain B884. However, the quality of bacteriocin (antimicrobial activity relative to the E. coli strain) with a lower productivity is higher for strain B2430. The minimum inhibitory concentration for the strains studied was: B2430 – 1.0-10⁸ CFU/ml, B884 – 1.0-10⁸ CFU/ml, B2455 – 1.0-10⁷ CFU/ml. The best indicator of the minimum inhibitory concentration was observed for strain B2430. Thus the strain B2430 had the greatest antimicrobial activity, it had an inhibitory effect on 12 test cultures: Escherichia coli, Alcaligenes faecalis, Candida albicans, Pseudomonas libanensis, Staphylococcus warneri, Erwinia aphidicola, Microbacterium foliorum, Bacillus licheniformis, Serratia plymuthica, Erwinia aphidicola, Bacillus endophyticus, Leucosporidium mesenteroides. Thus, among the test Lactobacillus strains, the strain of Lactobacillus paracasei B2430 is promising for further study.

Keywords: Lactic acid bacteria, bacteriocins, antimicrobial activity, biomass concentration, minimum inhibitory concentration

INTRODUCTION

Lactic acid bacteria (LAB) are a group of phylogenetically diverse gram-positive bacteria that have some common morphological characteristics, as well as metabolic and physiological features [1]. Lactic acid bacteria have GRAS safety status and are often used in the production of food products.

Lactic acid bacteria contain in human microbiota and have significant impact on human health [2, 3]. They produce a number of antimicrobial compounds, which include hydrogen peroxide, CO2, diacytal, acetaldehyde, lactic acid, D-isomers of amino acids, bacteriocins [4].

There is increasing tendency in our society to use more natural and safety products such as biodegradable materials, biofuels and different products, obtained by microbial synthesis (enzymes, polysaccharides, amino acids, vitamins, organic acids, bacteriocins) [5].

Bacteriocins are a heterogeneous group of ribosomally synthesized peptides or proteins that have antimicrobial activity against other bacteria. Action mechanism of bacteriocins is based on creation of
pores in the membrane of targeted cells, which interferes with the membrane potential and kills the cells. Bacteriocins are normally synthesized by strains as a defense system, and they inhibit development of microorganisms related to the producing strain [6]. Currently, one of the most urgent areas of research is the development of new antimicrobial agents, which is associated with a wide spread of pathogenic strains that are resistant to antibiotics [7]. In connection with this, in recent years, the interest of scientists in the study of bacteriocins has been especially increased, this is due to the possibility of their use as bioconservatives in food products in order to suppress development of pathogenic microflora [8, 9].

Bacteriocins are divided into separate classes. Lanbtiotics of the first class include lanbtiotics, which are small (< 10 kDa) thermally stable unmodified proteins. Second-class bacteriocins are divided into pediocin-like (subclass IIA) and bi-peptic bacteriocins (subclass IIb). The third class includes large (> 30 kDa) thermolabile proteins [10].

Due to the high antimicrobial potential of bacteriocins, their use is most common in medicine for the production of antimicrobial agents [11, 12]. Also bacteriocins may be used in the food industry for increasing the shelf life of products and providing food security [13, 14, 15]. The study of new types of bacteriocins is a topical issue in modern science, due to vast possibilities of their application, and in this connection this article is devoted to study of bacteriocins produced by lactic acid bacteria, the intensity of their production and the effectiveness of the action.

Thus, the study was intended to determine the intensity of bacteriocin production by the strains studied, as well as to determine the effectiveness of the action of bacteriocins against pathogenic strains to study the possibility of further use of bacteriocins.

**OBJECTS AND METHODS OF STUDY**

The following reagents were used as materials at different stages of the study: bacto-peptone, meat extract, citric acid ammonium (Component-Reactiv LLC, Russia); acetic sodium, sodium hydrogenphosphate (Belkhim LLC, Belarus); magnesium sulphate 7-water, manganese sulfate 5-water (Cation LLC, Russia); yeast extract, sodium chloride (Component-Reactiv LLC, Russia); Millex-GV filters (0.22 μm, Nihon "Millipore", USA), Müller-Hinton medium, Saburo medium (Lab-Biomed LLC, Russia).

Strains of microorganisms provided by VKPM FSUE "GosNIIgenetika" (http://www.genetika.ru/vkpm) were used as objects of study: Lactobacillus delbrueckii B2455, Lactobacillus paracasei B2430, Lactobacillus plantarum B884.

As test cultures, natural and medical strains of pathogenic microorganisms were used, which were designated as follows: No. 1 – Bacillus mycoides EMTC 9, No. 2 – Salmonella enterica ATCC 14028, No. 3 – Micrococcus luteus EMTC 1860, No. 4 – Escherichia coli ATCC 25922, No. 5 – Bacillus cereus EMTC 1949, No. 6 – Alcaligenes faecalis EMTC 1882, No. 7 – Proteus vulgaris ATCC 63, No. 8 – Pseudomonas fluorescens EMTC 42, No. 9 – Candida albicans EMTC 34, No. 10 – Pseudomonas aeruginosa ATCC 9027, No. 11 – Staphylococcus aureus ATCC 25923, No. 12 – Pseudomonas libanensis EMTC 1853, No. 13 – Staphylococcus warneri EMTC 1854, No. 14 – Erwinia aphidicola EMTC 1857, No. 15 – Microbacterium foliorum EMTC 1858, No. 16 – Bacillus licheniformis EMTC 1859, No. 17 – Serratia plymuthica EMTC 1861, No. 18 – Rahnella aquatilis EMTC 1862, No. 19 – Erwinia aphidicola EMTC 1863, No. 20 – Bacillus endophyticus EMTC 1864, No. 21 – Leuconostoc mesenteroides EMTC 1865, No. 22 – Enterococcus casseliflavus EMTC 1866.

All strains were cultured in a fermenter (80% filling) in a liquid MRS medium at 37°C for 3 days. The obtained biomass was separated from the culture medium by centrifugating at 8000 g for 20 minutes. A culture fluid filtered through 0.22 μm membrane filters was used as the bacteriocin solution. The resulting sterile solution of metabolites was used for experiments.

A suspension of nocturnal broth cultures grown on standard culture media was taken for work. The number of microorganisms (titre) in the suspension was determined by the optical density (OD) at a wavelength of 595 nm.

Biomass concentration was determined with the UV-1800 spectrophotometer (Shimadzu, Japan) by measuring the light absorbance at 595 nm. The obtained result was recalculated on the dry biomass basis. The cellular biomass was measured on a dry weight basis. Cells were precipitated on Buprog (pre-boiled) filters with a pore size of 0.24 μm, washed, dried at 80°C and weighed.

The protein concentration was determined spectrophotometrically by measuring the light absorbance at 595 nm. The obtained result was recalculated on the basis of the protein weight according to the albumin calibration table.

Specific productivity, as the value of the product increase per unit time, was determined by the formulas:

\[
Q_P(t_i) = \frac{P(t_i) - P(t_0)}{t_i - t_0}, \quad i = 1, 2, 3, \ldots,
\]

where \(t_i \in (0, \infty)\), \(t_0\) is a time at which the lag phase of the periodic cultivation process ends and exponential phase begins; it is obvious that \(Q_P(O) = 0\).

The suspension of overnight broth cultures of test strains grown on a standard culture media for 24 hours at a temperature of 37°C were used for the study. Cells from the agar surface were gathered with an inoculation loop and resuspended in NaCl solution to 0.5 units according to the McFarland standard. The test strains were grown in MRS broth for 24 hours at 37°C, then the culture fluid was centrifuged at 2000 rpm for 10 minutes and the supernatant fluid was separated. To separate cells, the supernatant fluid was filtered through Millex-GV filters. The culture fluid turbidity was adjusted to a value of 0.5 according to the McFarland standard (containing approximately
1.5 × 10⁶ CFU/ml). Suspension optical density was adjusted spectrophotometrically: light absorbance was within the same range as 0.5 in the McFarland units (at OD 450 nm, optical density was within 0.08–0.13). Then, the obtained microbial suspension was subjected to a series of 1:10 dilutions, thus reaching a metabolite concentration from 10⁻¹ to 10⁰ CFU/ml. 180 μl of the supernatant fluid of each test strain were added to the plate, then 20 μl of test culture strains were added to each of them. The plate was incubated at 37°C for 24 hours. 200 μl of sterile MRS broth and 180 μl of pure medium with 20 μl of each pathogen solution were used as controls. Bacterial growth was monitored by measuring the optical density during the culture process.

The culture media were prepared as follows: MRS medium, g/l: Bacto-peptone – 10.0; meat extract – 10.0; yeast extract – 5.0; glucose – 20.0; tween – 1.0; ammonium citrate – 2.0; sodium acetate – 5.0; sodium hydrogenphosphate – 2.0; magnesium sulphate 7-water – 0.1; manganese sulphate 5-water – 0.05. MRSA, dense medium, g/l: bacto-peptone – 10.0; meat extract – 10.0; yeast extract – 5.0; glucose – 20.0; tween – 1.0; ammonium citrate – 2.0; sodium acetate – 5.0; sodium hydrogenphosphate – 2.0; magnesium sulphate 7-water – 0.1; manganese sulphate 5-water – 0.05; agar – 20.0.

Antimicrobial activity of strains of lactic acid bacteria was additionally determined by means of agar-diffuse discs [16]. The test strain was plated on an agarized culture medium (MRSA) in the form of lawn and the lawn was covered with paper discs impregnated with lactic acid bacteria metabolites (10 μl/disc). Disc with MRS medium was used as a control, a disc with a ciprofloxacin antibiotic (from a standard kit) was used as a reference substance. The plates were incubated at 37°C for 24 hours. The results were taken into account by the presence and size (in mm) of the transparent zone of non-growth of microorganisms around the disc.

The minimum inhibitory concentration was determined with respect to the isolated strains of bacteria by the microtitration technique. The antimicrobial activity of the bacteriocins produced was evaluated relative to the strain of E. coli. A suspension of the E. coli strain without addition of bacteriocins was used as a control.

RESULTS AND DISCUSSION

The biomass concentration of strains of lactic acid bacteria and the activity of bacteriocins produced by them were determined by culturing in a MRS culture fluid, the study was carried out for 70 hours. The biomass concentration was determined spectrophotometrically. The antimicrobial activity of bacteriocins was determined by measuring inhibition zones, the study was carried out by a disc-diffusion test. The results obtained in the study of the dependence of concentration of bacteriocins and their activity on the culturing period are presented in Fig. 1–5.

The results obtained allowed to plot a chart showing the intensity of bacteriocins production during culturing of three test strains of lactic acid bacteria, as well as to show the intensity of use of bacteriocins from the culturing period for all three strains. Results are presented in Fig. 4–5.

When analyzing the results presented in Fig. 1–5, we concluded that the period of culturing at which the maximum bacteriocin concentration is observed and the duration at which their maximum antimicrobial activity is observed are different. Thus, the maximum concentration of bacteriocins in the culturing of strain B884 was observed with a culturing duration of 54 hours, while the maximum antimicrobial activity of this strain was observed with a culturing period of 18 hours. In strain B2430, the maximum concentration of bacteriocins was found during culturing for 44 hours, and the maximum activity was observed during culturing for 20 hours. For strain B2455, these values were 57 and 54 hours, respectively. To estimate the intensity of bacteriocin production by microbial strains, the productivity by the target product was calculated, which is defined as the magnitude of the product increase per unit time. The obtained results are represented in Table 1.
**Fig. 2.** Dependence of B2430 bacteriocins concentration and their activity on the culturing period: (1) protein concentration, (2) activity.

**Fig. 3.** Dependence of B2455 bacteriocins concentration and their activity on the culturing period: (1) protein concentration, (2) activity.

**Fig. 4.** Maximum intensity of bacteriocin production in the culturing of lactic acid bacteria: (1) B884, (2) B2430, (3) B2455.
**Fig. 5.** Dependence of the intensity of bacteriocin production on the lactic acid bacteria culturing period: (1) B884, (2) B2430, (3) B2455.

**Table 1.** Intensity of bacteriocin production in the course of culturing strains

<table>
<thead>
<tr>
<th>Strains</th>
<th>Inhibition zone, mm</th>
<th>Culturing period</th>
<th>Specific productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>B884</td>
<td>10</td>
<td>18</td>
<td>0.0141</td>
</tr>
<tr>
<td>B2430</td>
<td>11</td>
<td>20</td>
<td>0.0128</td>
</tr>
<tr>
<td>B2455</td>
<td>11</td>
<td>54</td>
<td>0.0046</td>
</tr>
</tbody>
</table>

When analyzing the data given in Table 1, we came to the conclusion that the following productivities were observed for the strains studied: B884 – 0.0141, B2430 – 0.0128, B2455 – 0.0046. In the B884 strain, the inhibition zone of the test culture was 10 mm, in the strains B2430 and B2455 – 11 mm.

The minimal inhibitory concentration of isolated strains was determined. The study was carried out according to the microtitration technique. The antimicrobial activity of the bacteriocins produced was evaluated relative to the strain of E. coli. The results of the study are presented in Table 2 and in Figures 6–8.

When analyzing the results obtained in determining the minimum inhibitory concentration, the following conclusion was made. With a bacteriocin concentration of strain B884 of 10⁸ CFU/ml, the growth of the E. coli B-6954 test strain was significantly lower compared to the control. With a concentration of 10⁷ CFU/ml, the growth of E. coli B-6954 is lower than in the control, up to and including 4 hours of culturing. At the remaining concentrations in the control sample, better indices were observed than in the samples with lactic acid bacteria. Thus, the minimum inhibitory concentration for strain B884 was 1.0·10⁸ CFU/ml.

With bacteriocin concentrations of strain B2430 from 1.0·10⁸ to 1.0·10⁶ CFU/ml, a less intensive growth of the test culture was observed than in the control. With a concentration of 1.0·10⁵ CFU/ml, the growth of E. coli B-6954 is lower than in the control, up to and including 4 hours of culturing. The minimum concentration of strain B2430 was 1.0·10⁶ CFU/ml.

When determining the minimum inhibitory concentration of strain B2455, it was found that at bacteriocin concentrations of 1.0·10⁸ and 1.0·10⁷ CFU/ml, the growth of the E. coli B-6954 test strain was significantly lower compared to the control. At a concentration of 1.0·10⁶ CFU/ml, the growth of E. coli B-6954 was lower than in the control, up to 6 hours of culturing inclusive, but with a culture time of 24 hours, the E. coli B-6954 concentration was higher than the control. The minimum inhibitory concentration of strain B2455 with respect to E. coli B-6954 was 1.0·10⁷ CFU/ml.

A study was made of the antimicrobial activity of bacteriocins produced by the strains under investigation, with respect to twenty-two pathogenic strains. The study was carried out by determining the optical density in a MRS culture fluid. The control sample was the culture of a pathogenic strain without the addition of bacteriocins. Results are presented in Fig. 9–11.
Table 2. Results of determination of the minimum inhibitory concentration of strains with respect to the strain *E. coli* B-6954

<table>
<thead>
<tr>
<th>Culturing period, hrs</th>
<th>Optical density of the mixture at different concentrations of lactic acid bacteria, CFU/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0⋅10⁸</td>
</tr>
<tr>
<td>B884</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.0651</td>
</tr>
<tr>
<td>2</td>
<td>0.0741</td>
</tr>
<tr>
<td>4</td>
<td>0.0934</td>
</tr>
<tr>
<td>6</td>
<td>0.1138</td>
</tr>
<tr>
<td>24</td>
<td>0.1215</td>
</tr>
<tr>
<td>B2430</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.0354</td>
</tr>
<tr>
<td>2</td>
<td>0.0400</td>
</tr>
<tr>
<td>4</td>
<td>0.0536</td>
</tr>
<tr>
<td>6</td>
<td>0.0876</td>
</tr>
<tr>
<td>24</td>
<td>0.1090</td>
</tr>
<tr>
<td>B2455</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.0556</td>
</tr>
<tr>
<td>2</td>
<td>0.0720</td>
</tr>
<tr>
<td>4</td>
<td>0.0954</td>
</tr>
<tr>
<td>6</td>
<td>0.1160</td>
</tr>
<tr>
<td>24</td>
<td>0.1236</td>
</tr>
</tbody>
</table>

Fig. 6. Change in optical density at different concentrations of bacteriocins of the strain B884, in relation to the test culture *E. coli*: (1) control, (2) 1.0⋅10⁸, (3) 1.0⋅10⁷, (4) 1.0⋅10⁶, (5) 1.0⋅10⁵.
Fig. 7. Change in optical density at different concentrations of bacteriocins of the strain B2430, in relation to the test culture *E. coli*: (1) control, (2) 1.0 \times 10^8, (3) 1.0 \times 10^7, (4) 1.0 \times 10^6, (5) 1.0 \times 10^5.

Fig. 8. Change in optical density at different concentrations of bacteriocins of the strain B2455, in relation to the test culture *E. coli*: (1) control, (2) 1.0 \times 10^8, (3) 1.0 \times 10^7, (4) 1.0 \times 10^6, (5) 1.0 \times 10^5.


DISCUSSION

Analysis of the results obtained in determining the intensity of bacteriocin production allowed to distinguish two strains: Lactobacillus plantarum B884 and Lactobacillus paracasei B2430, showed approximately the same results, but the quality of bacteriocin (antimicrobial activity relative to the strain E. coli) for strain Lactobacillus paracasei B2430 was higher.

For a more complete determination of the antimicrobial potential of bacteriocins synthesized by strains of lactic acid bacteria and selection of the most effective strain, a minimum inhibitory concentration of strains with respect to the strain E. coli. The following results were obtained: the minimum inhibitory concentration for the strain Lactobacillus plantarum B884 was 1.0·10^8 CFU/ml, for strain Lactobacillus paracasei B2430 – 1.0·10^6 CFU/ml, for strain Lactobacillus delbrueckii B2455 – 1.0·10^7 CFU/ml. Thus, the lowest inhibitory concentration was observed for the strain Lactobacillus paracasei B2430.

When analysing the antagonistic activity of the bacteriocins of the studied cultures with respect to the 22 cultures of pathogenic strains, it was concluded that bacteriocins of the strain Lactobacillus paracasei B2430 possessed the greatest spectrum of antimicrobial activity, as they inhibited the development of most test cultures, compared with the remaining strains and, in addition, this strain demonstrated the best properties and the degree of inhibition of the growth of pathogenic strains.

Based on the results obtained in the study of the intensity of bacteriocin synthesis and their effectiveness, they concluded that bacteriocins of the strain Lactobacillus paracasei B2430 have the greatest antimicrobial activity as compared with other strains of lactic acid bacteria, which implies that this strain is promising for further study.
REFERENCES


THE INFLUENCE OF STRUCTURAL AND KINEMATIC PARAMETERS OF THE MEAT GRINDERS ON ITS PRODUCTIVITY

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Abstract: Meat grinding tops are used in technological lines of production of sausages, canned meat and stuffed semi-finished products. An increase in the specific productivity of tops is economically sound which allows the consumer to reduce significantly the capital and operational costs. It has been established by the authors that not all the area of grating is supplied at any time with meat raw materials by means of the top screw, but only a certain sector is, which significantly reduces the productivity of the top. The researches have been performed using the mathematical modeling of the process of supply of meat raw materials in the top with the subsequent check of adequacy of mathematical model by means of natural experiments under production conditions. As a result, a mathematical model of process of supply of raw materials in the top has been developed that allows to increase significantly the accuracy of determination of its productivity and also to set the most rational structural and kinematic parameters of the working bodies of the top. It has been established that most of the volume of raw materials is supplied by the screw through the grinding knot. The presence of gratings and knives in the grinding knot and their geometrical parameters provide the formation of reverse flows of raw materials through a gap between the screw and the internal surface of the working cylinder and along the screw channel of the screw. The following optimum technological parameters of the process of supply of raw materials in the top have been determined: the outer diameter of the output grating is 0.15–0.155 m; the rotation frequency of the screw is 4.5–5.2 sec⁻¹; the angle of lead of rounds of the screw is 4.8–5.5 degrees; the area of frontal projection of a knife blade is 0.001–0.0011 m²; the thickness of the output grating is 0.0075–0.0082 m.

Keywords: Meat grinder, productivity, mathematical model, screw, grinding set

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INTRODUCTION

Meat grinding tops are used in technological lines of production of sausages, canned meat and stuffed semi-finished products. They are characterized by quite a simple design, safety in operation and low energy consumption. The most important technical indicator of tops is their productivity which defines a possibility of use of the machine as part of the designed processing line. The increase in productivity in practice is reached, most often, by an increase in the geometry of working bodies - gratings, knives and the screw. However, an increase in the specific productivity of tops is economically sound which allows the consumer to reduce significantly the capital and operational costs. Today the customary ways of increase in specific productivity (an increase in the rotation frequency of the screw, the application of gratings with larger holes, the use of trimmers) mostly exhausted their potential and do not allow to improve significantly the technical and economic indices of the machine.

An approach applied by most of researchers [1] when determining the productivity of the top is of interest in the context of this problem. According to it, the productivity of the top is determined by the formula

\[ G = f \ S_e \]

where \( S_e \) is screw efficiency (\( S_e = 0.25–0.35 \)). Such a low value of coefficient is explained [1] by the loss of raw materials through the gaps between the screw and a wall of the working cylinder, by slipping of raw materials during the rotation of the screw and so forth. However, in our opinion, the loss of about 70% of the greatest possible theoretical productivity is an excessively great value for the factors specified by the researchers.

The results of the authors’ researches [2] demonstrate the existence of the following features when supplying meat raw materials by means of the top of the screw - not all the area of grating is supplied at any time with meat raw materials by means of the top screw, but only a certain sector is which is
measured from the end of a round of the screw. It makes the productivity of the top twice as low [3]. In our opinion, this effect is the one that causes such a low value of screw efficiency \( S_E = 0.2 - 0.35 \) during the operation of the screw. The development of theoretical provisions and mathematical apparatus technique which would allow to determine the productivity of the top more precisely is urgent, considering all the necessary structural and kinematic parameters of the machine, and also the rheological parameters of raw materials.

Some approaches to the determination of productivity of the top are known. A number of researchers [1] suggest to determine the productivity of the top using the supplying ability of the screw or the grinding ability of the grinding knot. However these approaches cause considerable errors when making a calculation. The approach given in the works [4, 5] allows for more exact results. However it does not allow to display the above stated heterogeneity of supplying the work surface of gratings with raw materials. The approach offered by V. N. Potokin and N. A. Vishelevskiy offers to determine the productivity of the top when counting the pressure of supply of raw materials in the grinding knot of the top. The rheological properties of meat raw materials are described by V. V. Goryachev in the approach based on the provisions of the investigative theory of viscoelasticity. However such a technique of determination of productivity of the top does not allow to display the structural and kinematic parameters of the screw which essentially prevents it from being used in practice.

The purpose of the study is the development of a mathematical model of the process of supply of raw materials in the top which would allow to increase significantly the accuracy of determination of its productivity and also to set the most rational structural and kinematic parameters of the working bodies of the top.

**OBJECTS AND METHODS OF STUDY**

The researches were conducted using the mathematical modeling of the process of supply of meat raw materials in the top with the subsequent check of adequacy of mathematical model by means of natural experiments under production conditions.

The movement of raw materials in the working cylinder can be described by means of provisions of mechanics of continuous medium. At the same time the specific effect which consists in forcing raw materials only in a certain sector of cross section of the screw is expedient to be considered by means of the productivity coefficient \( K_Q \) (the physical sense of productivity coefficient \( K_Q \) is revealed in more detail in [6]). Then the productivity of the top is defined by the statement:

\[
G = K_Q (Q_{main} - Q_{s.c.} - Q_{s.c.}) \rho . \tag{1}
\]

where \( Q_{main} \) is the main flow of raw materials through the grinding knot, \( m^3/s \); \( Q_{s.c.} \) is a reverse flow of raw materials through the gap between the external surface of rounds of the screw and the internal surface of the working cylinder, \( m^3/s \); \( Q_{s.c.} \) is a reverse flow of raw materials along the screw channel of the screw, \( m^3/s \); \( \rho \) is the density of raw materials, \( kg/m^3 \).

Fig. 1 provides the design scheme of the top. It consists of the working cylinder 1 in which the screw 2 is set. Raw materials are supplied to the working cylinder from the bunker 3, and go out of the working cylinder through the grinding knot 4 in which they are ground.

The productivity of the top is defined, first of all, by the supplying ability of the screw which forms the main flow of raw materials \( Q_{s.c.} \) through the grinding knot. In the absence of the grinding knot the value of productivity of the top would be maximum at the output of the working cylinder (we consider that the working screw of the top is supplied with raw materials from the bunker constantly, the holes of gratings of the grinding set are not clogged with particles of raw materials, the gratings and knives are pointed properly, etc.). However the following major factors provide the reduction of productivity.

The presence of gratings and knives in the grinding knot and their corresponding geometrical parameters provide the formation of hydraulic resistance of the grinding knot \( P \), which prevents from the free effluence of raw materials from the working cylinder under the influence of the pressure produced by the screw. Thereof the reverse flows which characterize losses of productivity are formed: through the gap between the external surface of rounds of the screw and the internal surface of the working cylinder \( Q_{s.c.} \); along the screw channel of the screw between its rounds \( Q_{s.c.} \).
The mathematical description of movement of continuous medium (in this case – meat), can be obtained by the solution of system of the equations which consist of a continuity equation, a motion equation, an energy equation and equations of rheological condition of raw materials. At the same time, to obtain a rigorous solution of such a system of equations in case of supplying the curvilinear channel of the screw with real (with a rather complex set of properties) raw materials is a rather difficult task. However it can be simplified by adding certain assumptions and restrictions.

The rotating screw and the stationary working cylinder are replaced with a fixed screw and a rotating working cylinder. The screw channel which is formed by the space between screw rounds is straightened. That is instead of the rectangular-sectioned screw channel a straightened pipe the length of which is equal to the length of the screw channel is put, and which has a movable (according to the preliminary assumption) upper surface. The system of rectangular coordinates is chosen according to Fig. 1: The x-axis is along the channel, the axis y-axis is for the height, the z-axis is for the width of the channel.

Further the layer of raw materials which is limited within the enclosed volume to the sizes \( l_x, h_y, \) and \( L \) is considered. The density of raw materials \( \rho \), the speed of its motion along the axis of the channel \( \omega_0 \), the tensions \( p_0 \) which arise in raw materials (which are the result of acts of viscous forces), the pressure \( P \) and the temperature \( T \) are considered as functions of the time \( t \) and the spatial coordinates \( x, y \) and \( z \).

When solving problems of mechanics of continuous medium the following are unknown:
- Material density \( \rho = \rho \; t, x, y, z \);
- three components of velocity vectors along the axes of the chosen coordinate system:
  \[ u_x = u_x \; t, x, y, z \quad ; \quad u_y = u_y \; t, x, y, z \quad ; \quad u_z = u_z \; t, x, y, z \]  \( (2) \)
- six components of strain tensor (of ten components only six are independent owing to the symmetry of the tensor \( \rho_{ij} = \rho_{ji} \)):
  \[ \sigma_{xx} = \sigma_{xx} \; t, x, y, z \quad ; \quad \sigma_{yy} = \sigma_{yy} \; t, x, y, z \quad ; \quad \sigma_{zz} = \sigma_{zz} \; t, x, y, z \quad ; \quad \tau_{xy} = \tau_{xy} \; t, x, y, z \quad ; \quad \tau_{xz} = \tau_{xz} \; t, x, y, z \quad ; \quad \tau_{yz} = \tau_{yz} \; t, x, y, z \]  \( (3) \)

In the equations (3) the first index specifies a normal line to the platform in which this tension takes place, and the second specifies parallel to what axis this tension takes place. Thus, the normal tensions are designated as \( \sigma \), and tangents as \( \tau \);
- the temperature of the supplied raw materials – \( T = T \; t, x, y, z \).

To define these eleven unknown values it is necessary to make and solve the system consisting of the same quantity of equations:

- the continuity equation (the mathematical expression of law of perdurability of matter according to which the weight remains constant in the closed system):
  \[ \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho \cdot u_x) + \frac{\partial}{\partial y} (\rho \cdot u_y) + \frac{\partial}{\partial z} (\rho \cdot u_z) = 0 \]  \( (4) \)
- three motion equations in the chosen coordinate system (which are the mathematical formulation of Newton's second law):
  \[ \rho \left( \frac{\partial u_x}{\partial t} + u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + u_z \frac{\partial u_x}{\partial z} \right) = \rho \cdot F_x + \partial \sigma_{xx} + \partial \tau_{xy} + \partial \tau_{xz}, \]
  \[ \rho \left( \frac{\partial u_y}{\partial t} + u_x \frac{\partial u_y}{\partial x} + u_y \frac{\partial u_y}{\partial y} + u_z \frac{\partial u_y}{\partial z} \right) = \rho \cdot F_y + \partial \sigma_{yy} + \partial \tau_{xy} + \partial \tau_{yz}, \]
  \[ \rho \left( \frac{\partial u_z}{\partial t} + u_x \frac{\partial u_z}{\partial x} + u_y \frac{\partial u_z}{\partial y} + u_z \frac{\partial u_z}{\partial z} \right) = \rho \cdot F_z + \partial \sigma_{zz} + \partial \tau_{xz} + \partial \tau_{yz}. \]  \( (5) \)

where \( F_x, F_y, F_z \) are the projections of mass forces on to the axes of coordinates;
- six rheological equations connecting the components of tension tensor with the components of tensor of speeds of deformation of raw materials. This connection defines the rheological properties of raw materials;
- the energy equation.

To simplify the calculation when solving the system of equations the following admissible simplifications have been introduced. It is considered that an isothermal task should be considered which would provide an opportunity to do without the energy equation. The raw materials which do not compress, that is \( \rho = \text{const} \), should be considered. This simplification changes the type of continuity equation - if \( \rho = \text{const} \), then in that case \( \frac{\partial \rho}{\partial t} = 0 \), then it follows from the continuity equation that:
  \[ \rho \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) = 0 \]  \( (6) \)
and as \( \rho \neq 0 \), the continuity equation takes the following form:
  \[ \frac{\partial u_x}{\partial t} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0 \]  \( (7) \)

Analyzing the process of supply of raw materials in the top and the known rheological models of food media, we accept that the meat raw materials supplied by the top screw to its grinding knot is a viscoelastic medium the model of which consists of consistently connected bodies of Calvin and Maxwell. In that case the rheological properties of lumpy meat raw materials, according to [7], are displayed by means of the coefficient of viscoelastic properties:
\[
\psi = \frac{E_\mu \cdot E_5 \left(1 - e^{-\frac{t_1}{t_2}}\right)}{E_5 \left(1 - e^{-\frac{t_1}{t_2}}\right) + t_1 \cdot \eta_1 + E_\mu \left(1 - e^{-\frac{t_1}{t_2}}\right) + E_\mu \left(1 - e^{-\frac{t_1}{t_2}}\right)}, \quad (8)
\]

where \( E_\mu \) is the module of instant deformation of the body, Pa; \( E_5 \) is the module of equilibrium elasticity and after-effect, Pa; \( t_1 \) is the period of relaxation of tensions, sec; \( t_2 \) is an after-effect period, sec; \( \eta_1 \) is viscosity, Pa \cdot sec.

Then six rheological equations take the following form:

\[
\sigma_{xx} = -p + 2\psi \frac{\partial u_x}{\partial x}; \quad \tau_{xy} = \tau_{yx} = \psi\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right); \\
\sigma_{yy} = -p + 2\psi \frac{\partial u_y}{\partial y}; \quad \tau_{yz} = \tau_{zy} = \psi\left(\frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y}\right); \\
\sigma_{zz} = -p + 2\psi \frac{\partial u_z}{\partial z}; \quad \tau_{xz} = \tau_{zx} = \psi\left(\frac{\partial u_z}{\partial x} + \frac{\partial u_x}{\partial z}\right), \quad (9)
\]

where \( p \) is hydrostatic pressure:

\[
p = -\frac{1}{3} \left( p_{11} + p_{22} + p_{33} \right), \quad (10)
\]

here \( p_{11}, \ p_{22} \) and \( p_{33} \) are the main normal tensions.

The steady motion of medium (the stationary mode) exclusively of the start-up mode and the stop of the screw are being considered. This simplification results in the equality of derivatives of time to zero. For example, \( \frac{\partial u_x}{\partial t} = 0 \) etc. The mass forces are neglected, that is it is considered that \( F_x, F_y, \) and \( F_z \) are equal to zero in the equations (10). Gravity is not considered, meaning that the movement of raw materials occurs generally by means of other sources, for example, pressure difference. The speeds of movement of raw materials in the channels are rather small which allows to neglect the inertial loadings arising in motion, as well. The laminar flow which almost always takes place when supplying with high-viscosity media is being considered. In that case, in the absence of turbulence, of three components of speed of raw materials its component on the \( x \)-axis of the channel is the only that differs from zero – \( u_x \); \( u_y \) and \( u_z \) are considered equal to zero.

Thus, for the isothermal movement of medium in the steady mode, the possibility to neglect mass forces and lack of turbulence Navier-Stokes equation takes the following form:

\[
\frac{\partial \psi}{\partial t} + u_x \frac{\partial \psi}{\partial x} + u_y \frac{\partial \psi}{\partial y} + u_z \frac{\partial \psi}{\partial z} = F_x - \frac{1}{\rho} \frac{\partial p}{\partial x} + \psi \left( \frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right); \\
\frac{\partial \psi}{\partial t} + u_x \frac{\partial \psi}{\partial x} + u_y \frac{\partial \psi}{\partial y} + u_z \frac{\partial \psi}{\partial z} = F_y - \frac{1}{\rho} \frac{\partial p}{\partial y} + \psi \left( \frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} + \frac{\partial^2 u_y}{\partial z^2} \right); \\
\frac{\partial \psi}{\partial t} + u_x \frac{\partial \psi}{\partial x} + u_y \frac{\partial \psi}{\partial y} + u_z \frac{\partial \psi}{\partial z} = F_z - \frac{1}{\rho} \frac{\partial p}{\partial z} + \psi \left( \frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2} \right), \quad (11)
\]

After the substitution of the corresponding expressions in the equation (5) for the components of tension tensor from the equations (8) and the division of all of them by \( p \), three equations of movement of viscous medium written down in the form of Navier-Stokes equation have been obtained:

\[
0 = -\frac{1}{\rho} \frac{\partial p}{\partial x}; \quad 0 = -\frac{1}{\rho} \frac{\partial p}{\partial y}; \\
0 = -\frac{1}{\rho} \frac{\partial p}{\partial z} + \psi \left( \frac{\partial^2 u_x}{\partial z^2} + \frac{\partial^2 u_y}{\partial y^2} + \frac{\partial^2 u_z}{\partial x^2} \right), \quad (12)
\]

The analysis of equations (11) shows that the pressure \( p \) is constant throughout the section (it does not change on the \( y \)- and \( z \)-axes) and depends only on \( x \) and changes from section to section with changes of \( x \). In that case the partial derivative \( \frac{\partial p}{\partial x} \) is replaced with a full derivative \( dp/dx \) in the further calculations.

At the same time, assuming that \( u_x = u_y = 0, \frac{\partial u_x}{\partial z} = 0 \) has been obtained from the continuity equation (4). Therefore, unlike the pressure \( p \) the speed component \( u_x \) does not change from section to section, and there is only the function \( x, y \), i.e. it changes only throughout the section. Finally:

\[
u_x = u_x; \quad u_x \neq u_x; \quad p = p; \quad p \neq p; \quad x, y. \quad (13)
\]

The last of the equations (11) can be written down as:

\[
\frac{\partial^2 u_x}{\partial z^2} + \frac{\partial^2 u_x}{\partial y^2} = \frac{1}{\psi} \frac{\partial p}{\partial x}. \quad (14)
\]
If we consider that the change of pressure \( p \) along the length of the channel \( L \) is equal to \( \Delta p \), one equation in the form of Poisson’s equation can be obtained for the solution of problem of mechanics of continuous medium taking into account the made assumptions:

\[
\frac{\partial^2 u_x}{\partial z^2} + \frac{\partial^2 u_x}{\partial y^2} = -\frac{\Delta p}{\nu L}.
\]  

(15)

We accept that the delivery channel of the screw is rather small. Therefore, we can neglect the influence of sidewalls of rounds of the screw and consider that we deal with an infinitely narrow gap for which \( u_x \) does not change on the \( x \)-axis, that is \( \frac{\partial^2 u_x}{\partial x^2} = 0 \). Then Poisson’s equation will become still simpler:

\[
\frac{\partial^2 u_x}{\partial y^2} = -\frac{\Delta p}{\nu L}.
\]  

(16)

Using double integration on the \( y \)-axis and taking into account the boundary conditions ( \( \bar{u}_0 = \bar{u}_0 = 0; \; \bar{u}_0 = 0 \) ), the following will be obtained:

\[
\nu = \nu_0 - \frac{h_0 y - \frac{y^2}{2}}{2\Delta p} \frac{\partial p}{\partial x}.
\]

On the right side of this equation the first element is the speed of direct flow of raw materials along the screw channel of the screw (with the productivity \( Q_{main} \)), and the second element is the speed which is directed in the opposite direction, i.e. the reverse flow along the screw channel (with the productivity \( Q_{rev} \)). The sum of both speeds is the speed of net flow.

It follows from the equation (16) that if we integrate the speeds according to the section of the flow, in other words throughout the height \( h_1 \) and the width \( l_1 \), then the intensity of net flow (the amount of weight which passes along the screw per unit of time) will be stated for the bilamellate model using the formula:

\[
Q_{main} = \frac{\nu_0 h_1}{2} - \frac{l_1 h_1^3}{12\nu} \frac{\partial p}{\partial x}.
\]  

(17)

The first element in the right part of the formula (17) is the direct flow \( Q_{main} \), and the second is the reverse flow \( Q_{rev} \). At the same time, it should be noted that the influence of braking action of sidewalls of the pitch between the rounds of the screw on the flow is not taken into consideration.

Let us apply a change for the parameters which are part of the equation (17):

\[
\begin{align*}
\nu_0 &= \pi \cdot D \cdot n \cdot \cos \alpha; \\
l_1 &= \pi \cdot D \cdot \theta \cdot \alpha - l_1 \cdot \cos \alpha; \\
dz &= dl \cdot \sin \alpha;
\end{align*}
\]

where \( \alpha \) is the angle of lead of rounds of the screw.

Then the statement (17) of definition of intensity of net flow (without losses through the gap \( Q_{rev} \)) will be written as:

\[
Q_{main} = \frac{\pi \cdot D \cdot n \cdot \cos \alpha \cdot \pi \cdot D \cdot \sin \alpha \cdot l_1 \cdot \cos \alpha \cdot h_1}{12\nu} - \frac{\sin \alpha \cdot \pi \cdot D \cdot \sin \alpha \cdot l_1 \cdot \cos \alpha \cdot h_1^3}{12\nu} \frac{\partial p}{\partial l}.
\]  

(19)

Thus, the reverse flow is proportional to the hollow width, and also to the third degree of depth of round and is inversely proportional to the length of rectangular channel between the rounds.

We will obtain the statement of definition of intensity of flow of losses \( Q_{rev} \) through the gap between the screw and the working cylinder. This flow is considered as the one that passes through a rectangular slot with the sides \( \pi D / \cos \alpha \), \( \theta \) and \( b \cdot \cos \alpha \). This flow follows the equation (15) with the corresponding boundary conditions. At the same time, it is necessary to take into account that the reverse flow \( Q_{rev} \) in the gap is caused by a considerably greater pressure difference than the reverse flow \( Q_{rev} \) which is there in the screw channel. The values of pressure differences are related as the length of a pitch of the screw around to the thickness of a round.

Taking this into account:

\[
\pi \cdot D \cdot \cos \alpha \cdot b \cdot \cos \alpha = \pi \cdot D \cdot l_1 \cdot \cos \alpha.
\]  

(20)

Then we will obtain the statement similar to the statement of definition of reverse flow through the screw channel \( Q_{rev} \). The following replacements are only needed:

\[
\frac{\pi \cdot D}{\cos \alpha} \cdot b \cdot \cos \alpha = \frac{\pi \cdot D}{l_1 \cdot \cos \alpha}.
\]

(21)

It thus appears that we have the following:

\[
Q_{rev} = \frac{\pi^2 \cdot D^2 \cdot \sin^2 \theta \cdot \alpha \cdot \pi \cdot D \cdot \sin \alpha \cdot \cos \alpha \cdot \frac{dp}{dl}}{12\nu \cdot b}
\]  

(22)

For the purpose of practical application it is expedient to change a little the equations (19, 22) introducing, instead of the local pressure gradient \( dp/dl \) which is accepted constant throughout the length of the way of flow of mass of raw materials, the following value:

\[
\frac{dp}{dl} = \frac{p_2 - p_1}{L_{s,2}}.
\]

(23)

where \( p_1 \) is the weight pressure in the beginning of supply section; \( p_2 \) is the weight pressure in the end of supply section; \( L_{s,2} \) is the length of supply section.
Thus, the statements for the definition of separate components of net flow will take the following form:

- the direct flow along the screw type pump:

$$Q_{main} = \frac{\pi^2 \cdot D^2 \cdot n \cdot h_1 \cdot \sin \alpha \cdot \cos \alpha}{2};$$

(24)

- the reverse flow along the screw channel:

$$Q_{rev} = \frac{\pi \cdot D \cdot h_1 \cdot \sin^2 \alpha \cdot \frac{p_2 - p_1}{L_{1,2}};}{12\mu};$$

(25)

$$K_o = \frac{\beta_{max} \cdot 4\pi R^2 \cdot z_{act}^2}{\phi \cdot \cos \gamma_{mp} \cdot \sin \alpha \cdot \cos \alpha \cdot \cos \gamma_{mp}} \left(1 + \frac{q_o \cdot H_t}{k_t} + \frac{\left(1 - \frac{2\pi \cdot D \cdot h_1 \cdot \sin \alpha}{4\pi R^2 \cdot \cos \gamma_{mp}}\right)}{q_o \cdot k_t} \right) \times \left(1 + \frac{1 - \theta_B}{\phi} + \frac{q_s \cdot H_t}{k_t} + \frac{\left(1 - \frac{2\pi \cdot D \cdot h_1 \cdot \sin \alpha}{4\pi R^2 \cdot \cos \gamma_{mp}}\right)}{q_s \cdot k_t} \right),$$

(27)

where \(D_1\) is the outer diameter of the grating; \(d_h\) is the diameter of central hole of the grating; \(S_1^{max}\) is the area of the front projection of knife blade which is in the section of supply of raw materials contoured by the angle \(\beta_{max}\); \(z_{act}\) is the quantity of knife blades which are in the section of supply of raw materials contoured by the angle \(\beta_{max}\); \(k_{gr}\) is the empirical coefficient of increase in the resistance of grinding knot due to an increase in the distances between separate gratings by the values of thickness of knives the couples of grinders with gratings are composed of; \(\theta\) is the coefficient of utilization of working area of the initial grating; \(\theta_{pen}\) is the tension of penetration of raw materials when flowing around the jumpers between the holes of the grating, \(\phi\) is the resistance of grinding knot due to an increase in the speed of supply of raw materials the value of which depends on the lengthening of the holes of the grating and the type of raw materials; \(\alpha\) is the angle of friction of raw materials on the walls of the channel; \(\theta_{fr}\) is the tension of friction of raw materials on the surface of the screw; \(\theta_{fr}\) is the depth of the screw channel of the screw; \(n_r\) is the rotation frequency of the screw; \(H_{p-f}\) is a pitch between the rounds of the screw, within the last round; \(N_{act}\) is a pitch between the rounds of the screw when the coefficient of its filling with raw materials is equal to 1; \(\alpha\) is the angle of lead of rounds of the screw.

The experimental studies of accuracy of the mathematical model were performed in the sausage shop of the meat-processing enterprise LLC Cherkasskaya prodovol'stvennaya kompaniya. The objects of researches were the tops of the models K6-FVZP-200, VVS-180, MP-160 and AL-130 with the gratings with the outer diameter of respectively 200 mm, 180 mm, 160 mm and 130 mm. Fig. 3 provides the external view of the tops during the researches performed by the authors of the work.

Fig. 2. Design scheme of the last round of the screw (the front view) when determining the coefficient of productivity of the top and \(K_o\).

RESULTS AND DISCUSSION

According to the obtained results (Fig. 4), the above stated structural and kinematic parameters essentially influence the productivity of the top.

The increase in the outer diameter of grating \(D_1\) provides an increase in productivity due to the growth of quantity of holes for passing of raw materials (Fig. 4, a). Thus, with an increase in the diameter of the grating from 130 mm to 170 mm the productivity of the top increases by 2.3 times.

The increase in the angle of lead of rounds of the screw \(\alpha\) from 2º to 5º provides an increase in productivity up to 2 times (Fig. 4, b). At the same time the further increase \(\alpha\) provides the reduction of productivity of the top. It can be explained by the fact that the screw with a high value \(\alpha\) provides the movement of a portion of raw materials to a greater axial distance per one turn (in that case the productivity of the top increases).

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channel and through the gap between the screw and the cylinder. As a result, with low values of hydraulic resistance of the grinding knot (with the reduced values of $B_p$) the increase in $\alpha$ provides an increase in the productivity of the top (Fig. 4, c), and with the increased hydraulic resistance of the grinding knot (with the increased values of $B_g$) the increase in $\alpha$ provides a decrease in the production of the top.

For the tops which are designed for operation with the output gratings having small holes (the grinding of raw materials to the state of forcemeat) screws with $\alpha = 4-5^\circ$ can be recommended, and for the tops which are designed for operation with the output gratings having large holes (the grinding of raw materials to the state of meal) screws with $\alpha = 5.5-8^\circ$ can be recommended.

The influence of rotation frequency of the screw $n$ (Fig. 4, d) is similar to the influence of the angle of lead of rounds of the screw - with an increase in frequency the productivity first increases, reaches the maximum and then decreases. The maximum values of productivity are observed at $n=4-6$ sec$^{-1}$. The further increase in $n$ reduces productivity. It can be explained by the fact that to a higher speed of movement of raw materials through the holes of grating their higher hydraulic resistance corresponds. And it predetermines, among other things, an increase in the amount of raw materials which move between the rounds of the screw and through the gap between the screw and the cylinder backwards from the grinding knot which provides the reduction of productivity.

The increase in the thickness of the output grating $B_g$ provides the rapid reduction of productivity (Fig. 4, e). It is explained by the growth of hydraulic resistance of holes with an increase in their length (hydraulic resistance grows under the exponential law). As a result, with an increase in the thickness of the output grating from 8 mm to 20 mm the productivity decreases, depending on the type of raw materials, by 4.5–6.8 times.

The dependence of productivity of the top on the area $S_b$ of the frontal projection of blades of the knife which operates together with the output grating is inversely proportional (Fig. 4, f). In this case the reduction of productivity of the top with an increase in the total area of blades occurs due to the overlapping of a higher quantity of holes for the passing of raw materials.

![Fig. 3. Tops under study: (a) K6-FVZP-200, (b) VVS-180, (c) MP-160, (d) AL-130.](image-url)
Fig. 4. Dependence of the productivity of the meat grinder on its structural and kinematic parameters: (a) the outer diameter of grating; (b) the angle of lead of rounds of the screw, $B_g=0.016 \text{ m}$; (c) the angle of lead of rounds of the screw, $B_g=0.008 \text{ m}$; (d) the rotation frequency of the screw; (e) the thickness of the output grating; (f) the area of frontal projection of blades of the knife.
The performed studies have confirmed the results of mathematical modeling. The curves drawn according to the mathematical model are identical to the experimental ones, the error does not exceed 11%.

The productivity $G$, kg/h, was determined when revealing the rational parameters of process of grinding using the parameter of optimization:

$$G = f(D_g, n, \alpha, S_b, B_g),$$

where $D_g$ is the outer diameter of the output grating of the grinding knot; $n$ is the rotation frequency of the screw; $\alpha$ is the angle of lead of rounds of the screw; $S_b$ is the area of frontal projection of one knife blade; $B_g$ is the thickness of the initial grating of the grinding knot.

Due to the significant amount of factors in this case an expediently statistical analysis has been performed to obtain functional dependence in the form of multiple regression of the second order by means of central composite rotatable design (CCRD) of multiple-factor experiment. The method of CCRD allows to obtain more precisely the mathematical description of data distribution due to an increase in the number of experiments in the central points of plan matrix and the special choice of "star value".

The analysis of statistical characteristics of the obtained data has shown that the coefficients of their asymmetry tend to zero, that is the distribution of experimental data is symmetric and is approximated according to a normal law. The choice of ranges of variation of factors of functions was made in the way that their any combination provided by the plan of experiment could be realized within these intervals and did not provide contradictions. For this purpose searching experiments have been made to determine the areas in which the necessary combinations of levels of factors would be steadily realized. All the factors that are part of a searching function are the values that have different dimensions, and the values of these factors have various orders. Therefore, to obtain a response surface of these functions an operation of coding of factors has been performed, which is the linear transformation of factorial space.

It has been planned to obtain a multiple regression equation of the 2nd order:

$$y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{i,i} x_i^2 + \sum_{i=1}^{n} b_{i,i,j} x_i x_j, \quad (29)$$

where $y$ is one of high-quality functions; $b_i$ are the regression coefficients obtained using the method of the smallest squares.

For the assessment of adequacy of the obtained regression equation analytical and graphic methods of analysis have been used. The hypothesis of reproducibility of experiences is proved by means of Cochran’s criterion which shows that at the level of confidential probability of 95% dispersions are uniform because the design value of criterion is less than the tabular one. The assessment of importance of regression coefficients has been performed using Student criterion $t$. The assessment of adequacy of the obtained mathematical model has been performed using Fisher criterion which has shown that the design values are much lower than the critical ones, therefore the obtained regression model adequately describes the response surface, and it can be used for the optimization of the studied processes.

The analysis of distribution of the initial residues based on the predicted values has shown that they have a chaotic character of arrangement on the surface and there is no regularity in their behavior. Based on these observations, it is possible to draw a conclusion that the residues have no correlation relationships among themselves, that is the regression model sufficiently describes the interrelation of experimental values and is adequate.

Based on the results of the made experiments, studies and tests of the developed equipment for the process of grinding of meat raw materials, optimum technological parameters of its work (Table 1) the compromise value of which has been obtained using Cramer's method in the mathematical environment "MathCAD 15" have been determined (Fig. 5–7).

As a result of statistical optimization a correlation and regression equation of functional dependence of productivity of the process of supply of raw materials on constructive technology factors has been obtained. After processing of experimental data in the statistical environment STATISTICA 10.0 coefficients of complex equation of multiple regression of the 2nd order were obtained and the following dependence was derived:

$\begin{align*}
G &= -80127 + 702987D_g + 3249n + 3256\alpha + 1224813S_b + 2151062B_g - 2550000D_g^2 - \\
& - 367n^2 - 349\alpha^2 - 87187500S_b^2 - 88750000B_g^2 + 4750D_g n + 5125D_g \cdot \alpha + 2468750D_g \cdot S_b - \\
& - 812500D_g B_g + 4062n \cdot S_b - 33125n \cdot B_g - 19063\alpha \cdot S_b - 36250\alpha \cdot B_g.
\end{align*}$

\( (30) \)

Table 1. Optimum technological parameters of the studied grinding process

<table>
<thead>
<tr>
<th>Technological parameter</th>
<th>Rational value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer diameter of the output grating of the grinding knot, m</td>
<td>0.15–0.155</td>
</tr>
<tr>
<td>Rotation frequency of the screw, sec⁻¹</td>
<td>4.5–5.2</td>
</tr>
<tr>
<td>Angle of lead of rounds of the screw, degrees</td>
<td>4.8–5.5</td>
</tr>
<tr>
<td>Area of the frontal projection of one knife blade, m²</td>
<td>0.001–0.0011</td>
</tr>
<tr>
<td>Thickness of the initial grating of the grinding knot, m</td>
<td>0.0075–0.0082</td>
</tr>
</tbody>
</table>
Fig. 5. Surfaces of responses and their projections for productivity in the interaction of major factors: (a) the area of the front projection of one knife blade and the thickness of the initial grating; (b) the thickness of the initial grating and the angle of lead of rounds of the screw; (c) the area of the front projection of one knife blade and the angle of lead of rounds of the screw; (d) the thickness of the initial grating and the rotation frequency of the screw.
Fig. 6. Surfaces of responses and their projections for productivity in the interaction of major factors: (a) the area of the front projection of one knife blade and the rotation frequency of the screw; (b) the angle of lead of rounds of the screw and the rotation frequency of the screw; (c) the thickness of the initial grating and its outer diameter; (d) the area of the front projection of one knife blade and the outer diameter of the initial grating of the grinding knot.
As a result of the work, a mathematical model of the process of supply of raw materials in the top has been developed that allows to increase significantly the accuracy of determination of its productivity and also to set the most rational structural and kinematic parameters of the working bodies of the top.

By means of the obtained mathematical model the influence of structural and kinematic parameters of the top on its productivity has been studied. The model considers the phenomenon of supply of raw materials only in a certain sector of the last round of the screw of the top. It has been established that the productivity of the top is defined, first of all, by the supplying ability of the screw which forms the main flow of raw materials through the grinding knot. The presence of gratings and knives in the grinding knot and their corresponding geometrical parameters provide the formation of hydraulic resistance of the grinding knot which prevents from the free effluence of raw materials from the working cylinder under the influence of the pressure produced by the screw. Thereof the reverse flows of raw materials are formed characterizing losses of productivity - through the gap between the external surface of rounds of the screw and the internal surface of the working cylinder and along the screw channel of the screw. An essential increase in the productivity of the top can be reached increasing the rotation frequency of the screw, increasing its outer diameter, reducing the depth of a round, reducing the gap between the screw and the working cylinder, and also increasing the thickness of a screw round.

The following optimum technological parameters of the process of supply of raw materials in the top have been determined as a result of statistical optimization: the outer diameter of the output grating is 0.15–0.155 m; the rotation frequency of the screw is 4.5–5.2 sec⁻¹; the angle of lead of rounds of the screw is 4.8–5.5 degrees; the area of frontal projection of a knife blade is 0.001–0.0011 m²; the thickness of the output grating is 0.0075–0.0082 m.

The use of the obtained mathematical model allows to increase the accuracy of design calculations of tops and to prove new, highly productive, ways of supply of raw materials to the grinding knot of tops.

REFERENCES


ULTRAFILTRATION CONCENTRATING OF CURD WHEY AFTER ELECTROFLOTATION TREATMENT

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Abstract: This work offers a view on the outcomes of a study focusing on ultrafiltration of curd whey treated on the basis of the membrane electroflotation method in order to ensure more complete extraction of whey proteins when processing recoverable dairy crude. The feature that makes the method different is the presence of membranes between the anode and the cathode while the machines for membrane electroflotation are designed so that current does not run through the whey. To determine the element composition of whey prior to and after electroflotation the method of electron probe X-ray microanalysis was used. It has been shown that the filtration rate of whey treated through electroflotation nearly doubles up if compared to the initial rate. There has also been detected the dependence related to the impact that the concentration of solids and the pressure have on the filtration rate; besides, the kinetics of the ultrafiltration process has been investigated. The method of electron probe X-ray microanalysis was employed to study the element composition of whey both before and after the electroflotation treatment. The increase in the whey ultrafiltration rate after electroflotation can be explained by a growing Hydrogen index and a reduced concentration of Calcium after electroflotation. Besides, a quantitative physical model of whey ultrafiltration was developed, which takes into view specific features of polarization layer formation. The model implies conditional division of whey flow at the membrane surface into two streams – a normal one and a tangential one. Part of the protein molecules transported by the normal flow settles on the membrane surface while the other part of them remains near the surface up until it is pushed into the whey bulk by protein molecules of the tangential flow. That all mentioned above fixes certain elements of newness in the field of membrane technologies. The study was performed at the Voronezh State University of Engineering Technologies and the North Caucasus Federal University (Russian Federation).

Keywords: Whey, ultrafiltration, electroflotation, membrane technology


INTRODUCTION

Membrane technologies are the basis for low-waste and even non-waste (in case proper arrangements are made) dairy productions [1]. However, their wide implementation is limited, in particular due to low production capacity of membrane machines.

This also holds true for ultrafiltration separation of protein from milk whey [2]. Intensification of this process takes, first of all, minimization of protein deposit on the membrane surface. For instance, preliminary treatment of heated whey with ultrasound will reduce the membrane congestion and the amount of the protein deposit [3]. However, after numerous regular cleanings membranes increase their hydrodynamic resistance, which must be due to the fact that the pores get stuffed with protein from the inside surfaces [4].

If the impact of protein deposit could be minimized in any way, then concentration polarization will be the factor limiting the permeate flow through the membrane [5]. Thus, if for filtering sheep cheese whey membranes are used that are made of composite fluoropolymer, this allows a larger flow of permeate compared to polysulfone membranes, and protein deposits are minimum, while the dependency between the filtration rate...
and the pressure is typical of concentration polarization [6].

Whey acidity has a significant impact on the degree of protein deposit. The major role in reducing membrane permeation in case of changing pH belongs, obviously, to β-lactoglobulin. This is suggested with the following experimentally obtained data. In the pH range of 3.9–4.65, the filtration capacity goes down along with the growing pH [7]. At the same time, there is data [8] showing that under a decreasing hydrogen index down to pH 4.65, a high concentration and a low ionic strength of the solution, the solubility of β-lactoglobulin goes down sharply. The results obtained through scanning electron microscope investigation [9] suggest that filtration of β-lactoglobulin solutions leaves the membranes with some deposit appearing as thick layers. Transmission electron microscopy of membrane cross section [10] shows that similar deposits with incorporations of α-lactalbumin globules are also to be found in case of milk whey filtration. The pH range where the whey filtration rate is minimum (pH 4.6–5.5) is close to the range where isoelectric points of various β-lactoglobulins can be found (pI 4.9–5.4) [11, 12].

Since the pH of curd whey lies within this range, its ultrafiltration is more complicated than that of cheese whey. Neutralization of cheese whey with correcting chemical agents in most cases results in its reduced organoleptic features and increased allergenic capacity [13]. This is why there is a lot of interest taken in reducing curd whey acidity with electrophysical methods, e.g. electrodialysis [14] or membrane electroflootation. Membrane electroflootation is different from conventional electroflootation used for protein-containing solutions by the presence of a membrane between the cathode and the anode, while the machines themselves are arranged so that the electric current does not go through whey. Treatment this way improves the product’s organoleptic features, while the hydrogen index goes up as well [15].

Electroflootation results in 20–30% of protein eliminated from whey. One of the areas for using floated whey could be ultrafiltration treatment aiming at more thorough extraction of proteins. This is what the present work is focused on.

OBJECTS AND METHODS OF STUDY

In the ultrafiltration device used for the experiment, retentive mechanism/block moves round. There were track-etched polyethylene tetratraphtalate membranes used, with a pore diameter of 60 nm. The filtration rate of distilled water in the ultrafiltration cell was 12 ml/min (pressure – 0.2 MPa) (filtration rate her means the volume of filtrate that has passed through the membrane as per a single unit of time). The required level of pH, while the samples of whey were prepared, was reached through adding NaOH or HCl.

For electron probe X-ray microanalysis the whey was first dried, after which scanning electron microscopy was used to select several areas (0.2 mm) within the obtained powders for further microanalysis.

EXPERIMENT OUTCOMES

For 10 minutes following electroflootation, the whey pH goes up from 5.0 to 6.05. The filtration rate of whey that has been treated this way nearly doubles if compared to untreated whey (Fig. 1).

Further electroflootation whey treatment would not increase the filtration rate any more. The results obtained through the experiment indicate that there is a certain value in ultrafiltration of floated whey as well as in further research in the area.

Fig. 1 shows the dependence of curd whey filtration rate on the dry substance concentration, measured under pH = 4.8 and pH = 6.6. The charts demonstrate that the filtration rates at pH close to the values in Fig. 1 reveals a difference of 1.7 times.

Therefore, the filtration rate growth for the floated whey, if compared to the initial whey, is mostly due to a significant change in the whey hydrogen index through electroflootation. The smaller angles in the charts at 3–6% concentrations of dry substances mean that the 10–15% reduction in the protein concentration in the floated whey, if compared to the initial whey, has virtually no impact on the filtration rate. Therefore, it is most likely that there are two factors
that have an impact on the growth in the floated whey filtration rate. This, first of all, is due to the changing values of pH, while there is some extra impact added by the reducing concentration in Calcium ions.

Calcium ions present in whey are known to speed down its filtration rate [16]. Electron probe analysis done on the whey prior to, and following electroflotation showed a decrease in the Ca ion concentration in the floated whey (Table 1).

**Table 1. Whey element composition**

<table>
<thead>
<tr>
<th>Type of whey</th>
<th>Element, share,%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
</tr>
<tr>
<td>Floated whey</td>
<td>1.25</td>
</tr>
<tr>
<td>Non-floated whey</td>
<td>1.06</td>
</tr>
</tbody>
</table>

The difference in the filtration rate for wheys with various pH value remains in case of changing share of the dry substances in the solution, which should also be true for floated and non-floated wheys. With dry substances concentration tending towards zero, the graphs, as could be expected, tend to intersect. Figures 3 and 4 demonstrate the dependence of filtrate volume on time, and filtration rate on pressure, respectively.

**RESULTS AND DISCUSSION, PROCESS MODEL**

Fig. 3 shows that 20–30 seconds after filtration is started, the curve indicating the dependence between filtrate volume and time reaches the straight line portion, which means stable filtration rate.

---

**Fig. 3. Theoretical (1) and experimental (2) dependencies of filtrate volume of filtration time.**

The grades of the curves were used to determine the rate of steady filtration. At pH = 4.0 the steady rate was $v_s = 0.7$ ml/min; at pH = 10 $v_s = 1.2$ ml/min. Since the process stabilization time is much lower than that of measuring (5 min) in the previous experiments then the average filtration rate determined through these experiments can be considered close to the stable rate. Using the data of the electron microscopy [10] we can suggest that the sublayer with the $\alpha$-lactalbumin globules coating it, as well as the $\beta$-lactoglobulin layer above that, are developed within 20–30 sec.

Therefore, there is proof to the hypothesis stated in [11] and stating that globular formations of $\alpha$-lactalbumin, casein, and immunoglobulins may deposit on the membrane shaping some sort of bridges above pores, which later on host proteins that can develop layers.

The data obtained make it possible to assume that jellification process in a thick layer of $\beta$-lactoglobulin follows a mechanism that is different from, for instance, jellification in rather concentrated protein solutions. Actually, the induction period of jellification in the latest case is from several hours to several days, while it only takes dozens of seconds for gel to develop on a membrane.

This means that polarization layer development could be viewed not from the stance of gel formation yet similarly to particle deposition on solid bodies from gas phase, or in case of sedimentation deposition, from a liquid under the conditions of a tangential flow.

Let us make a conditional division breaking the flow of protein molecules approaching the membrane surface in two – a flow that is normal towards the membrane surface and a tangential one.

Each molecule of the normal flow, when approaching the surface, will stay there for a certain period of time $t_0$, until a connection develops between this molecule and other protein molecules. If, within this time, the molecule experiences an impact with a tangential flow molecule then it will be knocked out; however, if this impact takes place after the time of $t_0$ then it will get fixed on the surface and will not be knocked out. This metastable condition of a molecule may take place during filtration, unlike other processes of interaction between solutions and solid bodies, due to the fact that a large protein molecule will pressed against the surface with the water flow passing through the membrane.

Let us accept that each molecule of the tangential flow experiences a co-impact with a molecule from the normal flow, so the number of these molecules $N_t$ approaching a certain point at the surface within the time of $t$ shall be equal to the number of the co-impacts $N_c$ within the same period of time:

$$N_c = N_t.\tag{1}$$

Then, all the molecules of the perpendicular flow would approach the same point on the surface in a certain average piece of time $t_0$ that depends on the solution concentration and the velocity of the molecules $v_c$:

$$t_0 = \frac{1}{v_c^3 C_0}.\tag{2}$$

Since we are focusing on a thin layer of the liquid at the membrane surface, the concentration of $C_0$ in that might be taken as stable.

The period of time $t_2$, within which the tangential flow molecules reach point A, shall be expressed the following way:
\[ t_2 = \frac{1}{\nu_t \sqrt{C_0}}. \] (3)

Within time \( t \) the point \( A \) will be reached by the \( N_{\text{cross}} \) number of cross flow molecules:

\[ N_{\text{cross}} = \frac{t}{t_1}, \] (4)

as well as by those of the tangent ail flow \( N_i \):

\[ N_i = \frac{t}{t_2}. \] (5)

Now let us calculate the number of the molecules remaining on the surface as a result of impacts:

\[ N_{\text{rem}} = N_{\text{cross}} - N_i \cdot P, \] (6)

where \( P \) is the probability of an approaching molecule to be knocked out. Assume that within the time \( t_3 \), there were 10 molecules of the normal consequently approaching the boundary between impacts. The time for staying at the boundary for the first molecule is \( 10t_1 \), 2nd – 9\( t_1 \), the last one – \( t_1 \). Let us take \( \tau_0 = 3t_1 \). In this case the tenth, the ninth, and the eighth molecules may be knocked out at impact, while the others may not. The knock out probability \( P \) is:

\[ P = \frac{3}{10} = 0.3 = \frac{3t_1}{10t_1} = \frac{\tau_0}{10t_1}. \] (7)

Since 10 is the number of the molecules that approached the boundary within a time interval between the impacts, then:

\[ 10 = \frac{t_2}{t_1}, \] (8)

\[ P = \frac{\tau_0}{t_2}. \] (9)

In case the polarization layer is mostly developed faster than steady protein distribution takes place in the boundary layer, then the cross velocity of protein molecules \( v_c \) shall be approximately equal to the velocity of the filtrate flow passing through the membrane \( v_f \).

Using (2), (3), (4), (5), (9) in (6), in view of \( N_i = N \), we shall get:

\[ N_{\text{rem}}(t) = \left( v_f(t) \sqrt{C_0} - \frac{\tau_0}{t_2} \right). \] (10)

The developing polarization layer shapes, on the membrane surface, another membrane, through which whey is filtered.

In view of the hydraulic resistance and the membrane porosity, the Kozeny–Carman equation [17] could be modified as follows:

\[ v_f = \frac{\varepsilon_m k_0 \cdot P}{a_1 + 1}, \] (11)

where is the coefficient \( k_0 \) depends on the filtrate viscosity, the microstructure and porosity of the polarization layer, \( \varepsilon_m \) is the membrane porosity, \( a_1 \) is the parameter taking into account its hydraulic resistance.

Joining the polarization layer thickness \( l \) with the number of protein molecules that constitute it, we will have the following formula:

\[ l = \frac{m_p N_{\text{rem}}}{\rho \mu (S - S_{\text{por}})}. \] (12)

Where \( S \) is the area of the polarization layer, \( S_{\text{por}} \) is the total area of the pores that can be determined from the porosity of the polarization layer, \( m_p \) is the mass of a protein molecule, \( N_{\text{rem}} \) is the number of protein molecules, and \( \rho \) is its density.

Solving the equation system (10–12) regarding \( \nu_f \) in view of (3) we shall get:

\[ v_f = \frac{k_1 \rho}{\left[ -c + k \cdot \nu_f^2 \cdot t + \sqrt{\left( c + k \cdot \nu_f^2 \cdot t \right)^2 - 4t \left( k \cdot \nu_f^2 \cdot c - k_1 \rho \right)} \right]} + c. \] (13)

Here

\[ k = \sqrt{C_0^3 \cdot \tau_0^2}, \quad k_1 = \varepsilon_m \cdot k_0, \quad c = a_1 \cdot \rho \mu \frac{(S - S_{\text{por}})}{m_p}. \]

The formula below could be used to calculate the volume of the filtrate developing within the time \( t \) :

\[ V_f = \int_0^t k_1 \cdot \rho \cdot dy \left[ -\frac{\left( c + k \cdot \nu_f^2 \cdot y + \sqrt{\left( c + k \cdot \nu_f^2 \cdot y \right)^2 - 4y \left( k \cdot \nu_f^2 \cdot c - k_1 \rho \right)} \right)}{2} + c \right]. \] (14)
The dependence of the filtration rate on the pressure, as calculated following the formula (13), as well as the kinetic curve determined through integration of this formula, lay within satisfactory agreement with the experimental ones (Fig. 3, 4). More accurate data could be obtained taking into account the specific hydrodynamic features of whey flowing through a canal of a certain shape.

Fig. 4. Theoretical (1) and experimental (2) dependencies of filtration rate on pressure.

Let us accept that, following [18], the major role in $\beta$-lactoglobulin molecular interaction belongs to hydrophobic and electrostatic interactions, which may result in aggregation of proteins based o the mechanism described, for instance, in [19]. During that, the electrostatic interactions among protein globules are of local nature [20]. Then the condition for a molecule’s getting fixed in the polarization layer will imply three events coming simultaneously – a position of a proper molecule that would ensure its touching the polarization layer with the hydrophobic area; the presence of a hydrophobic area on such a molecule at the spot of contact with the polarization layer, and not very strong an electrostatic repulsion between the areas of globules approaching one another. In case the $\text{pH}$ of the solution is high enough, then the last condition often fails to be met, the time $\tau_0$ gets longer and, respectively, following (13), (14) the filtration rate is growing, which is observed in case of floated whey filtration. Electroflotation treatment for curd whey, which leads to a growth in the protein molecule negative charge, is likely to prove especially useful when using negatively charged membranes [21] that improve significantly ultrafiltration productivity. Due to a lower level of $\text{Ca}$ in concentrates of curd whey after it has been subjected to electroflotation treatment, they can be recommended to elderly people, since milk and dairy products may have a negative effect on the health in the elderly age, that is due to specific features about calcium absorption, which facilitates atherosclerosis [22].

CONCLUSION

The study has shown that there is a reason to conduct ultrafiltration concentration of curd whey after it has been subjected to electroflotation treatment.

Improved organoleptic properties of floated whey allow using ultrafiltration not only to produce whey protein concentrates with a high concentration factor, yet also to make base for yogurt, dairy drinks, and jellies with a higher content of whey proteins. At the same time it is possible not to exceed the concentration factor of 2–2.5, which reduces the load on the ultrafiltration equipment and decreases its elements, membranes first of all, contamination with protein.

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REFERENCES


DETERMINATION OF DEPENDENCE BETWEEN THERMOPHYSICAL PROPERTIES AND STRUCTURAL-AND-PHASE CHARACTERISTICS OF MOIST MATERIALS

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Abstract: Most of foods, raw materials and half-finished products are disperse systems. One of the most energy-consuming processes during foods production is drying. Intensive study of this process allows high-quality final products to be obtained at lower energy consumption. The aim of the research is to determine the interrelation between thermophysical properties and structural-and-phase characteristics of moist materials to establish optimum parameters for drying. A set of experiments has been made to find the influence of temperature on rheological properties of suspensions. A suspension of 40% chokeberry juice and ultradisperse starch from berry meal was used as the object of the research. Thermostatting was carried out in the range from 20 to 50°C with an increment of 10°C. The thermal conductivity coefficient for blocked samples with dimensions of 50x50x75 m³ was determined by means of a continuous plate flat source. Samples were prepared using the plastic mass forming method at the pressure of 50 MPa and the moisture of mass of 15%, and then dried. The results show that yield stress increases with temperature because of coagulation structuring intensification. The material has the highest thermal conductivity at the least capillary moisture of WLCM=14.2%, i.e. when a monomolecular layer of tightly bound water takes on the property of continuity through the material. The obtained results allow us to conclude that the use of volume phase characteristics makes it possible to improve the technique for determining thermophysical characteristics of dry and wet disperse systems to be improved, which in turn allows obtained results to be more accurate.

Keywords: Granulation, granules, powder, drying, phase characteristics

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INTRODUCTION

Dehydration is the main technological peculiarity when producing foods based on disperse systems. Water – together with smaller particles – forms suspensions and acts as a plasticizing agent during granule formation. Dehydration causes chemical, biochemical, rheological, mechanical and other changes in a material that in turn lead to mass and volume decreases, strength and lifetime increases, and etc. There are physicochemical, mechanical, thermal methods of dehydration [1]. The latter is more often being used to remove water from fine particle fractions.

A factor of drying is the partial pressure difference of vapour on the surface of the material being dried and in ambient medium [2]. The influence of operating parameters on the efficiency and time of drying, and the problems of product shrinkage and crack formation have been studied by such researchers as A.V. Lykov, A.S. Ginzburg, P.S. Kossovich, P.D. Lebedev, B.S. Szazhin, M.Yu. Lur’e, V.I. Mushtaev, B.N. Gak, O.S. Zaytsev [3].

The aim of the research is to determine the interrelation between thermophysical properties of moist materials and their structural-and-phase characteristics.

OBJECTS AND METHODS OF STUDY

In the theory of drying the object of the research are moist materials, their behavior during dehydration under different conditions and prediction of the process with time using drying sensitivity coefficients and crack formation criteria. These coefficients are calculated on the basis of mass balance using the weigh moisture content of materials. When drying free-disperse systems, e.g., wet berry meal, starch, and polysaccharide, it is enough to know mass balance of substances to describe drying. The case is different with structured disperse systems; apart from mass balance (sizes and geometrical form of particles are known preliminarily) total volume balance of mixture components should be used [4]. It is calculated according to the formula:

$$C_G + C_S + C_L = 1,$$

where $C_G$, $C_S$ and $C_L$ are volume concentrations of gas, solid and liquid phases.
The equation is valid throughout drying independently of materials properties and process rate. When moisture completely is removed, a three-phase system becomes a two-phase one; the following formula is true:

\[ C_t + C_s = 1. \] (2)

The use of phase characteristics of disperse systems allows us to evaluate the efficiency of dehydration and the quality of dried foods. At present, the latter is the main criteria for evaluating the former. Quality evaluation is performed visually taking into account the presence of cracks and the degree of linear and volumetric shrinkage [5].

Solid-phase volume concentrations should be used as the criteria to determine the efficiency of dehydration both under static conditions and during material structure forming. At present, mass and heat balances and Ramzin i-d diagram are used when studying drying [6, 7]. This technique allows us to determine the temperature of a drying agent and change in dried material moisture content during the process. Drying of shaped materials requires controlling of such parameters of drying agent as rate, temperature, moisture and geometry of material; it is frequently difficult to do this using the moisture content as a controlling parameter, therefore, the use of volumetric characteristic of the object is possible to exclude errors.

There is a strong relation between structure and phase characteristics of disperse systems. For example, a new system with quite new properties (flowability, homogeneity of material, plastic and strength properties) will be obtained as a result of drying of a two-component “solid – liquid” system. Rheological, structural and mechanical properties of the system and its formability can be predicted if material moisture, porous substance properties (fine particle fraction with high specific surface) and properties of structure-forming framework are known. The amount of liquid component in the system determines its strength and size of the formed crystallization structure; however, solid phase properties in the newly-formed disperse system do not influence the dependence between solid phase volume concentration and the material moisture content at \( W < W_{LCM} \), where \( W \) is the moisture of material and \( W_{LCM} \) is the least capillary moisture [5]:

\[ C_s = b \cdot W + a, \] (3)

where \( a \) and \( b \) are constants determined empirically.

Drying can be considered as a reverse process of mass forming, i.e. a disperse system consisting of continuous and solid phases; however, Eq. (3) would be valid as well at various factors of changes in material structure during drying. To determine these changes the difference in the processes mentioned should be considered [8]. Assume that a two-component system consists of a structural framework and a porous substance. The latter is fine dispersed particles which bind major part of water and, thereby, form a suspension. Coarse dispersed particles form a framework of a molding compounds and are not able to bind much water. Water-binding mechanism with a fine dispersed fraction having small median sizes has been studied by the following researchers [6]: B.V. Deryagin, A.V. Dumansky, M.H. Carapet’iants, N.N. Kruglitsky, S.P. Nichiporenko, G.V. Kukolev and others. The system consists of liquid and dispersed phases, water-binding capacity of the latter directly depends on its physical and chemical properties, e.g., a large-size starch granule has a layer-like structure, and its top layers are formed mainly by molecules of branch structure known as amylopectin [9]. The decrease of water content inside the starch granule causes pressure increase. As a result X-shaped cracks are formed on its surface. Starch is able to absorb up to 21% of water but only 6% is bound. When temperature increases up to 50–60°C starch granules tend to swell; water penetrates into macromolecules causing hydrogen bonds breakage. Apart from thermal treatment, starch swelling can be achieved by introduction of solutions with high pH (on the order of 10). Jellies contain acids however their concentration causes pH to be 4–7. This is an accepted value in food industry and does not affect the structural framework of granules [10]. Powdered sugar has more water-absorbing ability than starch granules, sucrose crystals are losing their strength when moisture is about 8%. We can conclude that suspension properties of molding compounds or granules depend on sorption activity, wetting ability, swelling ability, ion exchange ability and colloidal and chemical properties. Is should be noted that swelling ability is a essential parameter for forming structure during drying, as water removal from the system leads to volume decrease; i.e., the process is opposite to swelling [1].

Shrinking and swelling of a system takes much time, therefore, the optimum time of drying should be established to prepare the molding compound. It is not easily to perform because of operating costs. Drying is the most expensive process in instant beverage production. The increase of drying rate has both advantages and disadvantages. One of the disadvantages is crack formation, which disrupts obtained product structure [9]. Apart from that, increased temperature leads to increased solubility of such components as lactose, sucrose or fructose that gives rise to the increase of the liquid phase volume that in turn adversely affects obtained granules strength. Consequently, such variables as property of dried material, operating parameters and technical and economic characteristics should be taken into account when determining optimum parameters of drying [11].

Traditional technology of instant beverage production includes drying dump granules. During the process the suspension is heated. A number of experiments have been studied to establish the effect of temperature on rheological properties of the suspension. A suspension of 40% chokeberry juice and ultradisperse starch from berry meal was used as the object of the research. Thermostatting was carried out in the range from 20 to 50°C with an increment of 10°C. Time and conditions of preparing suspension samples were strictly observed and were constant. Table 1 gives rheological parameters of the system as a
function of temperature, where $\Theta$ is modulus of elasticity, $\eta$ is internal friction and $\Psi$ is sharing rate.

Table 1. Effect of temperature on rheological properties of suspension

<table>
<thead>
<tr>
<th>Rheological parameters</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>$\Theta$, dyne</td>
<td>270</td>
</tr>
<tr>
<td>$\eta_s$, poise</td>
<td>2.24</td>
</tr>
<tr>
<td>$\Psi_r$, $s^{-1}$</td>
<td>113</td>
</tr>
</tbody>
</table>

We can see that yield stress increases with temperature. That is because of coagulation structuring intensification. Viscosity value of the suspension changes twofold; similar situation is observed for water: the increase in temperature from 20 to 50°C reduces its viscosity from 0.001 Pa·s down to 0.00055 Pa·s. Solubility of sucrose in saturated solution of chokeberry juice rises by 25%, i.e., liquid phase volume increases. Taking into account changes in rheological parameters, it follows that plasticity rises sharply with temperature. In practice, we may observe it during the first stage of drying when granulate becomes softer. Dependences obtained can be true only for structured disperse systems that form the single pseudo phase.

Any material is capable of resistance to shrinking stress under certain conditions [12]:

1. The material must contain minimal amount of capillary moving water before drying. This will help to produce higher homogeneity and less material shrinking, and prevent transfer of soluble substances into the liquid phase.

2. Adhesive forces acting between structural framework particles must be equal to cohesion ones acting between particles of the suspension.

3. Whey proteins or surfactants should be used to obtain particles of molecular size which, thus, conduce the balance between adhesive and cohesive forces during drying.

4. Granulometric composition must insure particles to be packed tightly; this is achieved by structural framework and porous substance quantitative ratio.

5. It is necessary to reduce suspension shrinking in order to increase hardness of obtained granules during drying and the solid-phase volume concentration. It can be achieved by introduction of a small quantity of modified starch or protein (up to 1.5%). Molecules penetrate into space between large grains, thus limiting mobility of large grains [13].

6. Granulating should be performed at the drying temperature in order to decrease the volume of the liquid needed for coagulation to occur. Pellets formation process is attended by hydration; the amount of the liquid tends to be reduced, which provides hardness of granules.

Operating parameters of drying directly influence the crystallization rate of sucrose or lactose and the shrinkage of the material [14, 15, 16]. Drying regime, at which the decrease of the system volume is directly proportional to the increase of starch and meal volume during swelling, is the most optimum one. Shrinkage value depends on the drying rate. The higher operating parameters, the faster final shrinkage can be achieved. One should remember that shrinking will go on until capillary moving water is fully removed (even if volume shrinkage is stopped). Moreover, process rate effects distribution of temperature and moisture content across the material, especially for large cross-section granules. It implies irregular water distribution and shrinkage of layers during the process. Consequently, external layers reduce their volume, while internal ones keep their initial volume over time preventing granule shrinkage. It follows that tension forces act on the surface and compressing forces act inside. This leads to serious deformations and crack formation as a result. Professor A.F. Chizhsky has established the crack formation criterion based on the fact that an acting forces magnitude is proportional to the moisture difference between external and internal layers, product thickness being of no importance [17]:

$$\Delta W_{\text{max}} = W_{\text{AV}} - W_S,$$

where $\Delta W_{\text{max}}$ is the maximum allowed moisture difference, $\%$; $W_{\text{AV}}$ is the average moisture of the sample, $\%$; and $W_S$ is the moisture on the sample surface, $\%$.

For parabolic distribution of water, $\Delta W_{\text{max}}$ is equal (at constant rate of drying) to:

$$W_{\text{max}} = W_c - W_S,$$

where $W_c$ is the moisture in a central layer of the sample, $\%$.

Academician A.V. Lykov suggested dimensionless similarity criteria [7]:

$$K = \frac{(W_{\text{AV}} - W_S)}{W_{\text{in}}},$$

$$K_i = \frac{2(W_c - W_S)}{W_{\text{in}}},$$

where $K$ is the crack formation criterion, $\%$; $K_i$ is the Kirpichev’s mass exchange criterion; $W_{\text{in}}$ is the initial moisture of the material, $\%$.

M.S. Belopol’sky has proved that sensitivity of disperse mass to drying can be described by two coefficients for soft-mud molding products. The first coefficient describes formation of cracks on the surface during surface layer shrinking, while the second one describes formation of internal cracks on the final stage of its shrinking. The values in the expression for determining the sensitivity coefficient of disperse materials to drying characterize structural-and-mechanical and thermophysical properties of the system that effect crack formation.

There are a number of difficulties in describing the process by using differential equations of heat-and-moisture transfer. Therefore, it is more convenient to use such similarity criteria of heat-and-mass transfer as Lykov (Lu), Posnov (Pn), Kirpichev (Ki), Vio (Bi), Kossovich (Ko), Fourier (Fo), Rebinder (Rb) criteria.
Lykov criterion is an analogue of the Lewis number and characterizes the relation between heat and mass transfer in disperse systems. Mass transfer goes on faster than heat transfer if \( L_u > 1 \) [6]:

\[
L_u = \frac{a_m}{a_q},
\]

where \( a_m \) is the water conductivity coefficient, \( m^2/s \); \( a_q \) is the thermal diffusivity, \( m^2/s \).

Posnov criterion determines the relative fall of moisture content inside the material caused by temperature difference. In other words, the change in water potential depending on that of temperature is estimated [4].

\[
Pr = \frac{\delta \Delta \t}{\Delta u},
\]

where \( \delta \t \) is the thermal-gradient coefficient, \( kg/kg \cdot deg \); \( \Delta u \) is the temperature difference, \( deg \); and \( \Delta \) \( u \) is the moisture content difference, \( kg/kg \).

Kirpichev number characterizes the relation between intensity of internal and external moisture transfer [6]:

\[
K_i = \frac{j_m l}{a_m \rho \Delta \t},
\]

where \( j_m \) is the evaporation rate, \( kg/m^2 \cdot s \); \( l \) is geometric dimension, \( m \); and \( \rho \) is the liquid density, \( kg/m^3 \).

Vio criterion characterizes the ratio of heat input to the surface and heat output from the surface of the body to its inner layers due to thermal conductivity [7]:

\[
B_i = \frac{a_m l}{a_m \rho},
\]

where \( \beta_m \) is the mass exchange coefficient divided by the moisture content difference, \( m/s \).

Kossovich criterion shows the ratio of specific heat spent on evaporation of all moisture removed to specific heat used to heat up the moist material [6]:

\[
K_o = \frac{\tau \Delta u}{\tau \Delta \t},
\]

where \( r \) is the specific heat of evaporation, \( kJ/kg \); \( \tau \) is the specific heat capacity of the moist material, \( kJ/kg \cdot deg \).

Fourier criterion is a measure of heat saturation of the material and characterizes the process instability and governs change of moisture field \( (F_{om}) \) or temperature field \( (F_{Tm}) \) in the material with time [6, 7]:

\[
F_{om} = \frac{a_m \tau}{2l} \quad \text{or} \quad F_{Tm} = \frac{a_q \tau}{2l},
\]

where \( \tau \) is time, \( s \).

Rebinder criterion is the main parameter of drying kinetics determining the ratio of heat needed to heat up wet material to heat needed to evaporate moisture for infinitely small period [7, 8]:

\[
Rb = \frac{c \, dr}{\tau \, du},
\]

where \( c \) is the specific heat capacity of dry material, \( kJ/kg \cdot deg \); \( u \) is the average material moisture content, \( kg/kg \); and \( \tau \) is the average material temperature, \( deg \).

Analysis of parameters mentioned above lets us distinguish four groups of factors that influence drying: properties of liquid \( (\rho, r) \), properties of the material being dried \( (\tau, c, \beta_r, a_{m}, a_q) \), geometry of the body being dried \( (l) \), and operating drying parameters \( (j_m, u, t, \tau, \Delta u, \Delta \t) \). Two last factors effect irregularity in temperature fields and moisture content distribution across the material: the higher these parameters between the surface of the material and its center in the cross section, the more difficult to ensure continuity of the structure. Liquid component properties in the system influence energy consumption for its evaporation. Properties of the material being dried are characterized by its thermophysical characteristics but thermal diffusivity is more informative [7]:

\[
a_w = \frac{\lambda_w}{c_{pw} \rho_w},
\]

where \( a_w \) is the thermal diffusivity, \( m^2/s \); \( c_{pw} \) is the wet material heat capacity at constant pressure, \( kJ/kg \cdot deg \); \( \rho_w \) is the wet material density, \( kg/m^3 \); \( \lambda_w \) is the wet material thermal conductivity coefficient, \( W/m \cdot deg \); \( c_{pw}/\rho_w \) is the volume heat capacity, \( kJ/m \cdot deg \).

The thermal diffusivity in terms of physics is diffusivity of heat. According to eq. (15) and Fourier equation, molecular heat conduction \( q \) may be represented:

\[
q = -a_p \cdot \rho \nabla H.
\]

where \( a_p \) is the thermal diffusivity divided by enthalpy, and \( \nabla H \) is enthalpy gradient. Here, \( a_p \) is the diffusivity of enthalpy and \( c_p \cdot \rho \) characterizes heat-storage capacity of volume unit of the material. It implies that heat capacity should be determined as the sum of all volume fractions included in the wet material:

\[
c_w = c_s \cdot C_s + c_g \cdot C_g + c_L \cdot C_L,
\]

where \( c_s, c_g \) and \( c_L \) are specific heat of gas, solid and liquid phases.

It can be concluded that the thermal conductivity may be calculated in terms of additivity rule and its magnitude does not depend on mass of the material. Kirsher in his researches used follow formulas to determine the thermal conductivity coefficient [3]:

- for heat transfer along layers:

\[
\lambda_{mix} = \frac{1 - P}{\lambda_s + P \lambda_L},
\]

- for heat transfer across layers:

\[
\lambda_{mix} = \frac{\lambda_s \lambda_L}{1 - P}.
\]

where \( P \) is the porosity of layer; \( \lambda_s, \lambda_L, \lambda_{mix} \) are thermal conductivity coefficients of solid, liquid phases and their mixture.

Such Russian scientists as K.S. Krasnov, V.A. Lotov, and B.S. Sazhin suggested various dependencies to determine the thermal conductivity coefficient for moist disperse materials. It should be noted, however, that all of them are empirical because they do not make allowance for volume phase composition compared to Kircher formula. The last takes into account volume concentrations of liquid and
solid phases, nevertheless, the results may have some error. Consequently, the thermal conductivity coefficient of disperse materials should be calculated allowing for all phases volume presented in the system being subject to drying. According to the reference data, thermal conductivity of blocked food systems is within the range from 0.1 to 0.9 W/m·deg (these values for water and air are 0.58 and 0.023 W/m·deg, respectively). Volume fraction of each phase depends on their density, for example, low mass of gas phase has low density as well and occupies more volume in the system. Also gas phase has low thermal conductivity. It means that it will offer resistance to heat transfer during drying. Therefore, thermal conductivity directly depends on each phase volume concentration and their thermal resistance. Taking into account mentioned above, the thermal conductivity coefficient equation for disperse materials will take the following form:

\[
\lambda_w = \frac{c_S \lambda_S + c_L \lambda_L + c_G \lambda_G}{c_S + c_L + c_G} \quad (20)
\]

where \(\lambda_S\), \(\lambda_L\), \(\lambda_G\), \(\lambda_w\) are thermal conductivity coefficients of solid, liquid, gas phases and disperse material; and \(c_1\), \(c_2\), \(c_3\) are volume concentration factors of solid phase components. All of three phases are taken into consideration in the numerator, however, if \(c_L = 0\), it will include the ratio of solid and gas phases.

\[
\alpha_1 + \alpha_2 + \alpha_3 = 1 \quad (21)
\]

A number of experiments have made on a model mixture to determine the thermal conductivity coefficient to establish accuracy of eq. (20). Table 2 gives component composition of the mixture.

**Table 2.** Composition of studying mixture

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar</td>
<td>60</td>
</tr>
<tr>
<td>Starch</td>
<td>25</td>
</tr>
<tr>
<td>Chokeberry meal</td>
<td>15</td>
</tr>
<tr>
<td>Premixes</td>
<td>0.01 (above 100%)</td>
</tr>
</tbody>
</table>

The thermal conductivity coefficient for blocked samples with dimensions of 50 × 50 × 75 mm was determined by means of the continuous plate flat source. Samples were prepared using the plastic mass forming method at the pressure of 50 MPa; the moisture of the mass was 15%. After pressing, samples were subject to air drying and then inside the drier at the constant temperature of 60°C; further, samples have been cooled in the exicator up to 20°C for 24 hours. The thermal conductivity coefficient of the dry mixture was determined experimentally; its average value was 0.0696 W/m·deg. For the wet mixture, the thermal conductivity coefficient and the heat capacity factor were calculated using eq. (18), (19) on the basis of the data represented in Table 3 and obtained by calculation and experimentally.

According to the reference data, the heat capacity of solid, liquid and gas phases were taken 0.838, 4.19 and 1.005 kJ/kg K, respectively. The results are given in Table 4. Moisture conduction was computed from the capillary absorption coefficient \(K_{el}\) m²/s:

\[
W = 0.344 \cdot 10^6 K_{el} + 0.142, \quad (22)
\]

\[
C_S = -0.52 \cdot K_{el} + 0.74. \quad (23)
\]

**RESULTS AND DISCUSSION**

We can see from Table 4 that the capillary absorption coefficient equals zero if the moisture of the mixture is less than the least capillary moisture \(W_{el, CM}\) (0.142). This water can be removed by drying and Lykov criterion can be found when capillary moving water emerges, implying that \(W > W_{el, CM}\). If the moisture of the material is 19%, \(K_{el} = 1\) due to the equilibrium rate of iso-concentration and isothermal surfaces. These conditions are optimal for drying. However, at \(W > 0.19, Lu > 1\) implying that drying would proceed at constant rate and water diffusion rate would be higher than heat diffusion rate. Moreover, all energy supplied to the material is spent on water evaporation from the surface and energy movement from the center to the surface. It implies that when moving capillary water temperature in the center of the material would be much lower than drying temperature; the water movement process dominates. However, when capillary moving water would be removed, the temperature of the material would rise because of water evaporation from internal layers. Therefore, diffusivity dominates on this stage of drying. Figure 1 illustrates the relation between thermophysical properties and moisture content of the studied material.

**Table 3.** Calculated and experimental properties of studying mixture

<table>
<thead>
<tr>
<th>(W_r) rel. units</th>
<th>(P_{press}) MPa</th>
<th>(P_S) rel.</th>
<th>(P_L) rel.</th>
<th>(P_G) rel.</th>
<th>(C_S)</th>
<th>(C_L)</th>
<th>(C_G)</th>
<th>(C_L + C_G)</th>
<th>(C_S)</th>
<th>(S_{2/3}) cm²/cm³</th>
<th>(\delta_{envelope}) (10^5), m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.178</td>
<td>18.50</td>
<td>2047</td>
<td>1738</td>
<td>0.690</td>
<td>0.309</td>
<td>0.001</td>
<td>0.449</td>
<td>8816</td>
<td>5.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.203</td>
<td>8.80</td>
<td>2003</td>
<td>1665</td>
<td>0.661</td>
<td>0.338</td>
<td>0.001</td>
<td>0.513</td>
<td>8446</td>
<td>6.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.228</td>
<td>4.45</td>
<td>1955</td>
<td>1592</td>
<td>0.632</td>
<td>0.363</td>
<td>0.005</td>
<td>0.582</td>
<td>8076</td>
<td>7.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.245</td>
<td>3.50</td>
<td>1919</td>
<td>1542</td>
<td>0.612</td>
<td>0.378</td>
<td>0.010</td>
<td>0.634</td>
<td>7822</td>
<td>8.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.281</td>
<td>1.71</td>
<td>1835</td>
<td>1433</td>
<td>0.569</td>
<td>0.403</td>
<td>0.028</td>
<td>0.757</td>
<td>7269</td>
<td>10.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.307</td>
<td>1.45</td>
<td>1775</td>
<td>1358</td>
<td>0.539</td>
<td>0.417</td>
<td>0.044</td>
<td>0.855</td>
<td>6889</td>
<td>12.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.325</td>
<td>0.96</td>
<td>1726</td>
<td>1303</td>
<td>0.517</td>
<td>0.423</td>
<td>0.060</td>
<td>0.934</td>
<td>6610</td>
<td>14.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.350</td>
<td>0.70</td>
<td>1652</td>
<td>1224</td>
<td>0.486</td>
<td>0.429</td>
<td>0.085</td>
<td>1.057</td>
<td>6209</td>
<td>17.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.369</td>
<td>0.50</td>
<td>1607</td>
<td>1174</td>
<td>0.466</td>
<td>0.433</td>
<td>0.101</td>
<td>1.145</td>
<td>5955</td>
<td>19.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
According to Table 4, heat capacity of the studied mixture increases linearly up to its moisture optimal value (W = 0.24) and then heat capacity alters slightly, in spite of change in phase state of the material. This is because moisture content increases more intensively due to the fact that the liquid phase volume concentration alters more than that of solid phase since these phases have different density. Water has the highest heat capacity and with growing of hydration shells it would contribute increasing heat capacity until liquid layer thickness between particles reaches 1.5·10
^-7 m. It should be noted that flow of the liquid takes on the property of continuity over volume of the material. For the studied mixture, we can obtain water molecule diameter at W_{LCM} = 7·10^-7 m using the equation for calculating the water layer thickness on the particle surface and the data from Table 4; its value is 0.276 nm. It implies that at W_{LCM} the particle surface is capable of retaining of 700/0.276 ≈ 2500 molecular layers of water. The value is relative since some water is held in capillary envelope of production process.

For the first time the phenomenon was found by M.S. Metsik: under the influence of force field in solid phase, water molecules are oriented so that the layer of tightly bound water in the form of ice-like crystalline framework is formed. We can presuppose that molecular layers of water do not exhibit significant thermal resistance because of Brownian motion absence. It follows from Fig. 1 that the material has the maximum thermal conductivity at the least capillary moisture W_{LCM} = 14.2%, i.e. when a monomolecular layer of tightly bound water takes on the property of continuity over volume of the material. For the studied mixture, we can obtain water molecule diameter at W_{LCM} = 7·10^-7 m using the equation for calculating the water layer thickness on the particle surface and the data from Table 4; its value is 0.276 nm. It implies that at W_{LCM} the particle surface is capable of retaining of 700/0.276 ≈ 2500 molecular layers of water. The value is relative since some water is held in capillary vessels by capillary forces but it gives general understanding of increase in the least capillary moisture which characterizes quantitative and qualitative changes in the disperse system on any stage of production process.
On the basis of findings obtained we can conclude that the use of volume phase characteristics allows the technique for determining thermophysical characteristics of dry and wet disperse systems to be improved, which in turn allows the obtained results to be more accurate. It may be used for more detailed understanding of thermal conductivity of wet materials to predict both changes in thermophysical properties and behavior of different materials during process taking into account Lykov criterion. Mentioning different materials, we mean materials including different phase contents.

REFERENCES

STANDARDIZATION, CERTIFICATION, QUALITY AND SAFETY

IDENTIFICATION OF AROMATIC ALDEHYDES IN THE EXPRESS ASSESSMENT OF QUALITY OF HERBAL DISTILLED DRINKS

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Abstract: Despite a long study of main types of the herbs used in the Russian alcoholic beverage production, the structure of the components participating in the formation of "bouquet" of the alcoholic beverages obtained on their basis has not been studied yet. A study of content of aromatic aldehydes characteristic of distilled drinks in aqueous-alcoholic extracts of shell of pine nuts, common St. John's wort herb and wild camomile flowers, and also in the distilled drink simulated on the basis of these extracts became the purpose of this work. The raw materials obtained from the plants growing in the Altai Territory and the Altai Republic of the Russian Federation have been used for this work. The extracts were obtained by infusing the air and dry raw materials of the corresponding type in the 40% water solution of ethyl alcohol within 15 days at a temperature of 20 ± 2°C, with periodic agitation of extraction mixture, separation of extract by decantation and cleaning with filtering. The identification and quantitative determination of aromatic aldehydes were performed using the system of capillary electrophoresis "Kapel"-105M”. By the results of studies it has been established that the extracts differ, as for the content of aromatic aldehydes, both from the freshly obtained oak extracts and from the aged cognac distillates. A content of aldehydes has been revealed in the extracts of wild camomile flowers and St. John's wort herb at a level equal and higher than in the extract of shell of pine nuts within the total limits for the three considered extracts of, mg/dm²: for vanillin – from 18.5 to 96.4, for syringic aldehyde – from 8.5 to 19.4, for sinapic aldehyde – from 9.6 to 17.5, for coniferyl aldehyde – from 22.0 to 47.9. There is no direct correlation between the content of aromatic aldehydes in the imitated distilled drink and the content of these aldehydes in the initial extracts. The obtained data on the content of aromatic aldehydes in the nuts and herbs extracts are one of the evidence of similarity of the processes proceeding when obtaining these extracts and the processes that are the basis of technology of cognacs. In future, the obtained data can be put in a basis of techniques of express control of readiness of extracts and authenticity of new drinks in merchandising and technological practice.

Keywords: Alcoholic beverage products, cognacs, brandy, extracts of vegetable raw materials, pine (cedar) nuts, wild camomile, common St. John's wort, aromatic aldehydes, identification criteria

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INTRODUCTION

A natural consequence of development of the world consumer market of alcoholic products is the increase in the share of the forged drinks and the related search of new ways of prevention of possibility of realization of counterfeits. As for distilled drinks (cognacs, brandy, whisky etc.), this problem has managed to become a global trend as the market of these drinks mostly depends on the state of world economy and is rather unstable [1–3].

Distilled drinks are produced by means of the "enrichment” of distillates of grape wine, fermented fruit juices or aqueous-alcoholic infusions of vegetable raw materials. Such drinks are naturally enriched with volatile aromatic components – the products of biochemical and physical and chemical transformations of polyphenolic substances of vegetable raw materials (for the majority of distillates – oak wood) which considerably distinguishes them from other drinks with a high content of ethyl alcohol.

According to foreign experts, today the share of the forged production grows quicker than the alcohol market develops [4]. This relates to the fact that for the identification of cases of falsification and identification of authenticity of kind, age and the region of origin of the most branded distilled drinks the most modern
methods are applied: thin-layer [5], highly effective liquid [6, 7] and gas-liquid chromatography [8, 9], spectrophotometry [10], fluorescent [11] and chromatic mass spectrometry [12–14] and capillary electrophoresis [15, 16]. The existence and levels of content of such components of structure of drinks as highly volatile ethers [2, 12, 17], tannins and phenolic acids [2, 8], aromatic aldehydes [2, 5, 7, 16] and some ketones, aldehydes, alcohols and low-molecular volatile acids [12, 17–19] characteristic of distilled drinks are considered as the valid and potential criteria of authenticity. As one of the express methods of identification of the forged production it is also offered to use the dependence between the light absorption of test specimen in the infrared spectrum and a concrete type of drink – cognac, armagnac, brandy and others [10].

When searching new approaches to the assessment of authenticity and quality of alcoholic beverages the main attention has been paid for many years to the so-called aged distillates (cognacs, brandy, Calvados, whisky) – the most expensive drinks in the considered segment. The composition of aromatic components of cognacs and brandy as most known and popular drinks with consumers, has been studied in most detail: the main dependences of qualitative structure of aromatic components on the grade and the region of origin of wine material, on the duration of its contact with oak wood or oak staff have been described [17, 20]. Attempts to define the list of the most important substances forming the aromatic profile – the so-called "skeleton of aroma" of drinks [12, 18] have been made. In recent years great importance has been attached also to the search of methods of confirmation of authenticity for other distilled drinks: sherry, whisky, aromatic alcohols of juniper, tequila, mescal, absinthe, vermouths and some other drinks [21–26]. Studies concerning the further improvement of methods of control and identification of drinks fermented on the basis of vegetable raw materials [27, 28] also continue.

A feature of alcohol branch in Russia is the use of distilled drinks of more various vegetable raw materials (including wild-growing raw materials) in production, mainly in the form of extracts and infusions of the flowers, herbs and roots rich with polyphenolic compounds and ethereal oils. In this regard, most often extracts of pine nuts (Pinusibirica Du Tour) or their shell, extracts of wild camomile flowers (Chamomilla recutita (L.) Rauschert), common St. John's wort herb (Hypericum perforatum L.) and some other species of the plants, wild-growing and those which are specially cultivated for this purpose, are used.

The frequency of application of alcoholic beverages of pine nuts, camomile and common St. John's wort in domestic production is in many respects caused by the fact that the extracts on their basis allow to "smooth" the sharp taste and smell of ethyl alcohol in drinks and to give a characteristic color tone and gloss close to cognac to the finished goods. In turn, the composition of volatile components of these raw materials provides the unique identity of aroma of the obtained drinks.

The analysis of literary data shows that the chemical composition of pine nuts (shell and perikernel film) is slightly similar to oak wood as for the content of polyphenolic substances and lignin [29]. According to the classical technology of cognac production, it is the most important extractive substances that go through hydrolysis and ethanolysis to aromatic aldehydes in the course of ageing cognac materials and necessary for the formation of unique "bouquet" of cognac wine materials and ready-for-use drinks. Besides, as it is noted in some works, there are compounds in the structure of aromatic components of cognacs – in particular, scopoletin, that give a resinous cedar shade of "old" drink to the "bouquet" and a taste of the aged cognacs [30, 31]. The noted data explain to some extent the range of application of pine nuts in the production of Russian alcohol products and cause the theoretical possibility of their use when obtaining the drinks similar to cognac distillates [32, 33].

When studying the properties and composition structure of volatile components of aqueous-alcoholic extracts of wild camomile flowers and common St. John's wort herb the main attention is traditionally paid to the composition of terpenes and the polyphenolic compounds various in structure and properties. Among terpenes and polyphenolic compounds, the flavonoids, phenolic acids and anthracene derivatives [34–37] causing the therapeutic properties of the medicinal and cosmetic preparations produced on the basis of these plants by a lot of Russian enterprises are considered to be the most important ones. However the literary data on the existence of aliphatic alcohols, aldehydes, ketones and average esters in the composition of extracts of wild camomile flowers and common St. John's wort herb allow to assume a possibility of formation of more complex compounds including those which have an aromatic molecular structure in the course of extraction, as well.

It is necessary to know the content of the most characteristic compounds the number of which in the drink can also change with its age to authenticate the falsification of a drink.

When authenticating cognac production the confirmation of duration of contact with oak wood determined by the results of analysis of volatile and nonvolatile components is considered to be the major feature.

The main processes in the formation of the volatile compounds characteristic of cognac distillates and necessary for the formation of the "bouquet" typical for cognacs and brandy, include the processes of oxidation of tannins and lignin.

Aromatic aldehydes (Fig. 1) and the products of their subsequent oxidation – aromatic acids – make up to 30% of the polyphenolic complex of cognac distillates and the cognacs aged in contact with oak wood. At the same time, the content of vanillin in cognacs can vary from 0.2 to 2.4 mg/dm³, the content of sinapic and coniferylic aldehydes is 0.3–2.4 mg/dm³ and 0.3–2.6 mg/dm³ respectively. The content of syringic aldehyde – to 7.8 mg/dm³ of drink [38] can be the most considerable.

The data on the composition of aromatic aldehydes in the aqueous-alcoholic infusions and extracts on the basis of pine nuts or their shell, wild camomile flowers,
common St. John’s wort herb and many other types of the vegetable raw materials traditional for domestic alcoholic beverage products, are not available in Russian and foreign literature. In this regard a study of aromatic aldehydes in the extracts obtained from the types of vegetable raw materials which are most popular with the industry and an assessment of the possibility use of these data in merchandising and technological practice for the identification and control of quality of drinks on the basis of such extracts seem appropriate.

The purpose of work is the research of composition and content of the main aromatic aldehydes in the aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John’s wort herb for the identification of these substances in the composition of new distilled drinks.

The following tasks act as solvable in the work:
– the systematization of literary data on the content of aromatic aldehydes in cognac distillates;
– the determination of content of aromatic aldehydes in the composition of aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John’s wort herb and the comparative analysis of the obtained results with the literary data on cognac wine materials;
– the assessment of possibility of use of the data on the content of aromatic aldehydes in the studied aqueous-alcoholic extracts in merchandising and technological practice of identification and control of quality of distilled drinks of various producers.

OBJECTS AND METHODS OF STUDY

The following is used as the study object:
– raw materials – the pine nuts prepared in the cedar forests of the Republic of Altai (Pinus sibirica Du Tour) and their shell, wild camomile flowers (Chamomilla recutita (L.) Rauschert) and common St. John’s wort herb (Hypéricum perforatum L.) prepared in the Biysk district of Altai Krai;
– the aqueous-alcoholic (40% vol.) extracts of shell of pine nuts, wild camomile flowers and common St. John’s wort herb;
– the imitation of distilled drink – the blend made by mixing of the obtained aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John’s wort herb according to the receipt given below.

Study methods. Methods of data collection and processing, of comparative analysis and systematization of information from scientific publications and periodicals were used when studying the literary data.

The aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John’s wort herb were obtained infusing the air and dry raw materials of the corresponding type in the 40% aqueous solution of ethyl rectified alcohol within 15 days (the conditions of extraction had been chosen earlier, by the results of preliminary studies [39]) at a temperature of 20 ± 2°C, with periodic shaking of the extraction mixture and the separation of the obtained infusion (extract) by decantation with the subsequent filtering through the paper filter of the brand “White Ribbon”.

The ratio raw materials : extragent was chosen by the results of patent search and was 1 : 3 during the extraction of shell of pine nuts, and 1 : 10 for wild camomile flowers and common St. John’s wort herb.

The experimental blend of aqueous-alcoholic extracts – an imitation of distilled drink – was prepared by mixing of individual extracts in the ratios providing a characteristic golden and cognac color with “gloss” (see Photo 1) and the aroma of drink close to the cognac one.
The receipt of experimental blend:  
– an extract of shell of pine nuts – 91.2 dL;  
– an extract of wild camomile flowers – 25.4 dL;  
– an extract of common St. John's wort herb – 12.4 dL;  
– a water solution of ethyl rectified alcohol, 40% vol. – 871 dL.

The total of tannins in the extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb was determined in terms of gallic acid according to the method of HPLC using the chromatograph "Waters-Alliance" (USA) with a spectrophotometric detector M 2998.

The identification and quantitative determination of aromatic aldehydes in the individual extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb were performed in 3 weeks after preparation using the technique M 04–53–2008 [40] based on the system of capillary electrophoresis "Kapel'-105M" (Russia) in the mode of direct detecting with the use of universal borax buffer (0.02 M solution).

The injection of test specimen was performed under conditions recommended by the technique [40]: under the pressure of 30 Mbar for 20 sec. Analysis conditions: the wavelength is 373 nanometers, the temperature is 20°C, the voltage is +25 kV; the analysis duration is 10 minutes.

Characteristics of the capillary: the internal diameter is 75 microns, the effective length is 50 cm, the total length is 60 cm. Calculation method: absolute calibration with the use of standard samples of vanillin, sinapic, coniferyl and syringic aldehydes (the standards of Aldrich, Fluka). The identification of peaks was performed using the method of addition of standard samples.

Under similar conditions the analysis of experimental blend of aqueous-alcoholic extracts was performed, also in 3 weeks after its preparation.

The studies were repeated 3–4 times. The processing of experimental data was performed with the use of IBM PC with the Elforan software (Lumex Group).

RESULTS AND DISCUSSION

According to the literary data, the accumulation of aromatic aldehydes in the distilled drinks like cognac, brandy and whisky is determined by the degree and rate of degradation of lignin of oak wood. It is shown that the maximum rate of decay of lignin is in the distillates with the content of ethyl alcohol of 80% vol., but the maximum concentration of aromatic aldehydes has been recorded in the distillates with the content of ethanol of 65% vol. [38].

At the initial stages of ageing of cognac alcohols there are processes of hydrolysis and ethanolysis of lignin with the transition to the aqueous-alcoholic solution of extractive substances and the formation of sinapic and coniferyl aldehydes. Afterwards there is a process of "saturation of ethylenic bonds" and the formation of syringic aldehyde and vanillin the further oxidation of which produces syringic and vanillic acids [41]. The described sequence of stages is also confirmed during lignin oxidation by chemical means [42]. And if the content of highly volatile aromatic volatile compounds – aliphatic alcohols, ethyl aldehyde, volatile acids and esters – depends in many respects on the ampelography of the grapes [17] processed for alcohol, then the content of aromatic aldehydes in cognac wine materials is substantially interrelated with the type and geography of growth of oak [43, 44] as the source of the extractive substances which are transformed to aromatic components of cognacs in the course of their ageing.

In cognac wine materials all aromatic aldehydes begin to collect during their first year of ageing in contact with oak wood, with a steady tendency to the accumulation of their total content with an increase in the ageing period. It is offered to use the intensity of the chromatographic peak of the syringic aldehyde prevailing in the composition of aromatic aldehydes, that reflects its concentration and is in direct correlation with ageing duration as the "age index" of cognacs and brandy. The value of this index, as a rule, does not exceed 1 for ordinary cognacs and brandy, and it can reach 9 for branded and collection ones [6].

The nature of accumulation of individual aldehydes is considered a feature of no less importance: for vanillin, coniferyl and syringic aldehydes an exact dynamics has been established that reflects a continuous increase in their concentration to a certain age of cognac alcohol after which a reverse trend of slow decrease is observed [1]. One of the natural consequences of these processes is the change of ratio of syringic aldehyde and vanillin in the course of ageing of distillate reaching 2–4 for collection cognacs [6].

Despite long studies in this regard, the published literary data on the content and ratio of aromatic aldehydes in cognacs and cognac semi-finished products are still rather contradictory. The information on the content of vanillin in cognacs and cognac distillates and the possible dependence of content of total and individual aromatic aldehydes, as well as the products of their further oxidation, on the duration of ageing and concentration of distillate (Table 1) is especially ambiguous.

For other drinks of the group of distillates data on the regularities of accumulation of aromatic aldehydes are not provided in scientific literature. At the same time, when obtaining infusions and extracts of vegetable raw materials for blends of alcoholic beverage products in Russia lower concentrations of ethyl alcohol, within 35–50% vol., are used. The choice of extragents in such concentrations is caused by the fact that in these conditions the maximum of the polyphenols [32, 33] that give an attractive color to the extracts and have at the same time a high antioxidant activity are derived [45].
Table 1. Content of phenolic substances and aromatic aldehydes in the aqueous-alcoholic extracts of oak wood and the cognac distillates of different ageing periods (the ageing from 2.5 to 15 years)

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Concentration of aldehydes / Data source</th>
<th>in cognac distillates</th>
<th>in extracts, mg/g of raw materials [43]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[6]</td>
<td>[7]</td>
</tr>
<tr>
<td>Total of phenolic substances, g/dm³</td>
<td>not applicable</td>
<td>0.398–1.013</td>
<td>not applicable</td>
</tr>
<tr>
<td>Vanillin, mg/dm³ (peak areas in the HPLC)</td>
<td>0.1–1.6 (2–0.4)</td>
<td>0.19–2.41 (10.7)</td>
<td>2.053–3.953 (10–7)</td>
</tr>
<tr>
<td>Siringic aldehyde, mg/dm³</td>
<td>0.2–2.8 (2–0.6)</td>
<td>0.63–7.84 (10.7)</td>
<td>2.275–7.533 (10–7)</td>
</tr>
<tr>
<td>Sinapic aldehyde, mg/dm³</td>
<td>0.5–2.4 (2–0.6)</td>
<td>0.33–0.87 (10.7)</td>
<td>not applicable</td>
</tr>
<tr>
<td>Coniferylic aldehyde, mg/dm³</td>
<td>0.9–2.6 (2–0.6)</td>
<td>0.26–0.79 (10.7)</td>
<td>0.587–1.668 (10–7)</td>
</tr>
<tr>
<td>Syringic aldehyde / vanillin ratio</td>
<td>2–4 : 1 (2–0.3)</td>
<td>2 : 1 (2–0.2)</td>
<td>2–4 : 1 (2–0.3)</td>
</tr>
</tbody>
</table>

Note. * Data are provided for waterless alcohol.

When receiving extracts from the studied raw materials it is necessary to consider the features of their morphology. The features of morphology of the considered raw materials consist in the following:

– the shell of pine nuts needs 1 year to be formed and is rich with lignin, as well as oak wood is;
– camomile flowers need no more than one month to be formed and are not rich with lignin;
– common St. John's wort herb and blooms need from two to three months to accumulate lignin before the end of blossom time.

Taking into account the features of morphology of the considered raw materials, it is possible to assume that the rate of stages of degradation of lignin and accumulation of aromatic compounds under conditions of receiving extracts from the shell of pine nuts, wild camomile flowers and common St. John's wort herb should be the same (for example, in the extracts of shell of pine nuts), or higher than that of the similar processes in cognac wine materials.

It is also possible to assume the participation of the polyphenolic compounds of extracts of nuts and herbs with a lower molecular weight which constitute more than 50% of extractive substances of these raw materials in the processes of hydrolysis, ethanolysis and oxidation [32, 36, 46]. In particular – tannins (Table 2) with the prevalence of hydrolyzed substances which are part of them [37, 47]. Therefore, it is possible to predict both the equal, and a higher content of aromatic aldehydes in the studied extracts and various alcoholic beverages made on their basis.

The electrophoregrams given in Figures 1–3 show the composition of aromatic aldehydes in the aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb. The analysis of electrophoregrams and the comparison of the obtained results (Table 3) to the literary data shows that the content of aromatic aldehydes in the undiluted extracts exceeds the levels of content of the corresponding aldehydes in the cognac distillates of different ages (Table 1).

Fig. 1. Electrophoregram of aqueous-alcoholic extract of shell of pine nuts (2-time dilution).
No doubt, the choice of extraction module with an increase of which a higher gradient of concentration of lignin containing material on the surface and, respectively, a higher speed of biochemical processes of hydrolysis and the subsequent oxidation of extractive polyphenolic substances is provided is of great importance in the achievement of similar levels of content of aromatic substances in extracts.

It is authentically established that, as for four analyzed aromatic aldehydes, all the three extracts differ both from the freshly obtained oak wood extracts [43], and from the aged cognac distillates. Despite the forecasts, a content of aldehydes at the level equal or even higher than in the extract of shell of pine nuts has been revealed in the extracts of wild camomile flowers and common St. John's wort herb. Vanillin is the strongly prevailing aldehyde in the composition of extract of wild camomile flowers (96.42 ± 9.64 mg/dm³), the ratio of syringic aldehyde : vanillin in the extract shifts to 1:5. In the extract of

![Graph](image-url)

**Fig. 2.** Electrophoregram of aqueous-alcoholic extract of wild camomile flowers (2-time dilution).

![Graph](image-url)

**Fig. 3.** Electrophoregram of aqueous-alcoholic extract of common St. John's wort herb (4-time dilution).

**Table 2.** Content of total of tannins in the extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb

<table>
<thead>
<tr>
<th>Extract</th>
<th>Content of total of tannins (Data of the authors of the article, mg/dm³ of the extract)</th>
<th>Reference data [Source]</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pinus sibirica</em> shell</td>
<td>0.07 ± 0.01</td>
<td>1.5–3.0% in the extract [29]</td>
</tr>
<tr>
<td><em>Hypéricum perforatum</em> herbs</td>
<td>0.48 ± 0.05</td>
<td>10.3–12% in the raw materials [37]</td>
</tr>
<tr>
<td><em>Chamomilla recutita</em> flowers</td>
<td>0.34 ± 0.04</td>
<td>not applicable</td>
</tr>
</tbody>
</table>
common St. John's wort herb, on the contrary, a precursor of vanillin — coniferyl aldehyde (47.88 ± 4.80 mg/dm³) prevails.

The extract of shell of pine nuts for which the established ratio of syringic aldehyde: vanillin is mostly approximated to the corresponding value for cognac distillates and is 1:2.3 can be considered the most balanced as for the ratio of the noted aromatic aldehydes.

It is also necessary to note that there is no direct correlation between the content of aromatic aldehydes in the experimental mixture of extracts — an imitation of distilled drink (Fig. 4) and the content of these aldehydes in the initial extracts (Table 3). Presumably, processes of the second oxidation stage, with the formation of products of oxidation of aromatic aldehydes, first of all — vanillin which is formed of coniferyl aldehyde continued in the simulated drink within three weeks before performing an electrophoretic study.

As an alternative hypothesis, it is also possible to consider the oxidation of aromatic aldehydes to syringic and vanillic acids continuing in the blend. In particular, the actual concentration of syringic aldehyde in the experimental blend is the basis of the similar hypothesis. At the same time, this hypothesis demands additional instrument-based confirmation — a study of composition of aromatic acids in the individual extracts and the experimental blend.

It is known that vanillin and syringic aldehyde have a more characteristic and intensive aroma than their predecessors — coniferyl and sinapic aldehydes, and give pleasant vanilla tones to drinks [38]. The threshold concentration of smell with the concentration of ethyl alcohol in the drink of 40% vol. for vanillin is 0.01 mg/dm³, and the threshold of taste in cognac alcohols is 0.1 mg/dm³. The increase in the concentration of vanillin to 30 mg/dm³ provides the distortion and deterioration in the taste and aroma of drink. The threshold concentration of aroma and taste for coniferyl aldehyde is 3 and 10 mg/dm³ respectively, for syringic aldehyde is 50 and 100 mg/dm³. Sinapic aldehyde can be felt only with the concentration of no less than 200 mg/dm³ [38]. Therefore, taking into account the obtained results and threshold concentrations of taste and smell of individual aromatic aldehydes, the aqueous-alcoholic extracts of the vegetable raw materials considered in the work can be used for the direct simulation of taste and "bouquet" of alcoholic beverages.

![Fig. 4. Electrophoregram of experimental mixture of extracts – imitation of distilled drink.](image)

| Table 3. Content of characteristic aromatic aldehydes in the aqueous-alcoholic extracts of vegetable raw materials and the experimental blend (an imitation of distilled drink) |
|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| Aldehyde                                | Concentration of aldehydes, mg/dm³          |                                              |                                              |
|                                           | in aqueous-alcoholic extracts in a blend of extracts |                                              |                                              |
|                                           | *Pinus sibirica shell* | *Chamomilla recutita flowers* | *Hypéricum perforatum herbs* | design* | actual |
| Vanillin                                | 20.00 ± 1.95 | 96.42 ± 9.64 | 18.52 ± 1.85 | 4.51 ± 0.45 | 13.22 ± 1.30 |
| Syringic aldehyde                       | 8.55 ± 0.90 | 19.36 ± 1.94 | 10.91 ± 1.10 | 1.41 ± 0.15 | 0.69 ± 0.14 |
| Sinapic aldehyde                        | 17.55 ± 1.80 | 12.42 ± 1.24 | 9.65 ± 1.00 | 2.03 ± 0.20 | 5.12 ± 0.62 |
| Coniferyl aldehyde                      | 22.04 ± 2.20 | 29.40 ± 2.94 | 47.88 ± 4.80 | 3.35 ± 0.32 | 0.35 ± 0.03 |
| Syringic aldehyde / vanillin ratio      | 1 : 2.3 | 1 : 5 | 1 : 1.7 | 1 : 3.2 | 1 : 19 |

*Note. * The value is calculated on the basis of experimental data on the content of aromatic aldehydes in individual extracts taking into account their prescription dosage when obtaining a blend (see Study methods).
Taking into account that in the course of storage of distilled drinks the hydrolysis and oxidation of polyphenolic compounds and aromatic aldehydes continue, it is possible in our case to predict a further increase in the content of syringic aldehyde and vanillin in the drinks on the basis of the extracts considered in this article. The character and dynamics of these processes demand a further study.

CONCLUSIONS AND RECOMMENDATIONS

The obtained data on the content of aromatic aldehydes in the extracts are one of the evidence of similarity of the processes proceeding when receiving extracts from nuts and herbs, and the processes making a basis of technology of cognac production. The submitted data on the content of aromatic aldehydes in the considered extracts can be used for the direct simulation of “bouquet” of distilled drinks on their basis [48]. In the long term, the obtained data can be put in a basis of techniques of technological express control of readiness of aqueous-alcoholic extracts and authenticity of new drinks in investigation practice.

The existence of four characteristic aromatic aldehydes and other volatile components inherent in cognac production in the composition of the studied extracts testifies to a potential possibility of substitution of cognac distillates to cheaper raw components. In this regard there is a need of collection of information and formation of special statistical database on the structure and content of aromatic aldehydes in extracts and finished goods on the basis of vegetable raw materials which are widely used by Russian enterprises when producing drinks of the distillates group.

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PHYSICAL AND CHEMICAL INDICATORS AND MERCHANDASING ASSESSMENT OF WILD STRAWBERRY, GOOSEBERRY, CHERRY, RASPBERRY, BANANA, WILD ROSE AND KIWI

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Abstract: The fruit and berry vegetable raw materials applied in food production technologies have a positive impact on the consumer properties of ready-made product. The qualitative composition and the quantitative content of separate elements in fruit and berry raw materials have been studied in the work (wild strawberry, gooseberry, cherry, raspberry, banana, wild rose and kiwi). The studied samples conformed to the requirements of standards in appearance, coloring, taste and smell. Physical and chemical indicators, such as the content of solids, sugars, pectinaceous substances, organic acids, the titratable acidity of the crude and processed fruit and berry raw materials have been defined. It has been established that the highest quantity of carbohydrates, including sucrose, is in bananas, the lowest quantity is in raspberry. There is no sucrose in wild strawberry and wild rose. Cellulose is in all fruit and berry raw materials, its highest content is in raspberry. Pectinaceous substances are mainly in gooseberry. It has been established that all fruit and berry raw materials are rich with organic acids, except bananas. Apple acid is the only that prevails in bananas. At the same time the acidity of bananas is low. The titratable acidity of wild strawberry is the highest which is proved by the fact of lack of sucrose in it. It has been shown that fruit and berry raw materials contain such vitamins as B₁, B₂, B₆, PP, β-carotene, K₁, E and C. The greatest amount of vitamin C is in wild rose, there are also a lot of group B vitamins in wild rose, tocopherols prevail in wild rose and gooseberry. All types of fruit and berry raw materials are rich with major macro - and microelements. It follows from the obtained data that the physical and chemical indicators can not be the objective criteria of identification of the crude and processed fruit and berry raw materials as their values for different types of raw materials are very close, and sometimes they coincide. Some indicators, such as the content of vitamin C and total of carotinoids can indirectly be suitable for the identification of group of fruit and berry raw materials, but they do not allow to define a type of fruit and berry raw materials.

Keywords: Fruit and berry raw materials, quality, organoleptic properties, physical and chemical properties, identification


INTRODUCTION

The fruit and berry vegetable raw materials applied in food production technologies have a positive impact on the consumer properties of ready-made product. In particular, it favorably affects the organoleptic characteristics of finished goods: taste, aroma and color. At the same time the vegetable components play a role of natural dyes and fragrances. Thanks to the presence of biologically active agents, fruit and berry vegetable raw materials have a good effect on the human body [1, 2].

Merchandising characteristics of fruit and berry raw materials: the high nutrition and biological value, the simplicity in the preparation for production, the wide range of fruits and berries and their derived products allow to use them effectively in various food technologies, including dairy products technologies [3].

The studied fruits and berries as vegetable objects with the prevalence of water in their composition have no high calorific value: 100 g of the edible part give only 30–100 kcal [4]. Easily digested carbohydrates prevailing in the dry weight are the main energy-yielding material in the composition of fruits and berries. Fruits and berries are of the highest value in nutrition as a source of biologically active agents - vitamins, macro- and microelements, specific substances and food fibers. Thanks to the presence of the listed groups of compounds, fruits and berries improve digestion, the activity of cardiovascular system, the neuroemotional state of the person, therefore a lot of fruits and berries are irreplaceable in nutrition. The average annual need of the person for fruits and berries is 7 kg. [4].

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Fruits and berries, first of all, are an effective source of various carbohydrates among which there are sugars, polyols, pectinaceous substances, cellulose and hemicellulose. Sugars are digestible carbohydrates – glucose, fructose, sucrose because of a sweet taste inherent in them. The total content of sugars is from 1.0 to 20% [5, 6, 7]. Monosugars, glucose and fructose prevail. Their content is approximately equal in a lot of fruits and berries. The amount of sucrose (disaccharide) does not exceed 1% in the majority of them. Fructose – the sweetest and most dietary valuable sugar which is expedient for use in the diets with a low caloric content, and also in the food of children and diabetics prevails in the composition of raspberry. Pectinaceous substances and cellulose are carbohydrate polymers, they are not digestible for the human body, but their physiological role is high enough. Pectinaceous substances are part of cells and noncellular clusters. These are derivatives of galacturonic acid. There is soluble pectin and insoluble pectin (protopectin) [8, 9]. The ratio between soluble pectin and propectin in the composition of fruits and berries changes in the course of growth, maturing and storage. Therefore, changes of consistence become noticeable as well. The content of pectinaceous substances with high jellifying properties which are shown at a certain ratio of pectinaceous substances, sugar and acids [10] in fruits and berries is 0.2–1.8%.

The purpose of work consisted in the determination of parameters of quality of fruit and berry raw materials. The study problems included the determination of titratable acidity, content of vitamins and minerals and also toxic components in fruit and berry raw materials.

**OBJECTS AND METHODS OF STUDY**

In accordance with the purpose and tasks of the work, the study objects were the following:

- fruit and berry raw materials:
  - *Rubus idaeus* (raspberry, the grade “Nagrada”),
  - *Fragaria vesca* (remontant wild strawberry, the grade “Berdskaya rannyaya”),
  - *Ribes sibira-crispa* (garden gooseberry, the grade “Koopetor”),
  - *Punus fruticoso* (ground cherry, the grade “Altyayskaya lastochka”),
  - *Rosa majalis Herrm* (cinnamon rose),
  - *Actinidia delicosa* (kiwi delicatessen),
  - *Musa paradisiaca* (banana of “extra” grade);
- model fruit and berry mixtures.

All fruit raw materials used in the work were studied upon the organoleptic and physical and chemical indicators of quality according to the requirements of the relevant normative documents.

The test specimens were selected in accordance with GOST 26313-84 “Products of fruit and vegetable processing. Acceptance rules and methods of sampling”. The raw materials are mixed and the single samples are selected from different layers of a product by means of a scoop, a sampler, a siphon and so forth, weighing 100–500 g each. The number of single samples from each unit of transport packing must be not less than two. The total weight of specimen from each selected unit of transport packing must be from 0.3 to 3.0 kg depending on the weight of the product needed for the tests.

The fruits of raspberry were assessed for the compliance with the requirements of GOST R 54691-2011. The appearance, maturity degree, state, smell and taste of berries, the presence of the agricultural fruits and berries damaged by agricultural depredators, the rotten and spoiled berries are assessed in an organoleptic way [11, 12].

The indicators of quality of fruits of wild strawberry were assessed in accordance with GOST 6828-89. The appearance, maturity degree, taste and smell, the presence of the sick and damaged berries of wild strawberry are determined in an organoleptic way; the size of berries - by measuring to a precision of no more than 0.1 mm [13].

Each fraction was weighed. All weightings were performed to a precision of no more than 0.01 kg.

**RESULTS AND DISCUSSION**

Table 1 presents the carbohydrate composition of fruits and berries.

The analysis of tabular data allows to draw a conclusion that the highest quantity of carbohydrates, including sucrose, is in bananas and the lowest is in raspberry. There is no sucrose in wild strawberry and wild rose. Cellulose is in all fruit and berry raw materials, its highest content is in raspberry. Pectinaceous substances are mainly in gooseberry.

Table 2 presents the titratable acidity and qualitative composition of organic acids of the studied fruits and berries, Table 3 – the content of vitamins.

Fruits and berries are a source of the mineral substances playing an important role in metabolic processes. The total of mineral substances or ash in the composition is 0.2–0.54%. Macro-, micro- and ultramicroelements are found in the composition of ash.

Analyzing these tables, it is possible to note that all fruit and berry raw materials are rich with organic acids, except bananas. Apple acid is the only that prevails in bananas. At the same time the acidity of bananas is low. It is explained by the existence of a large amount of sucrose. The titratable acidity of wild strawberry is the highest which is proved by the fact of lack of sucrose in it.

The qualitative composition and the quantitative content of separate elements are different which is caused by their biological and specific features to accumulate elements, the provision of soils with available forms of elements. In some cases the mineral composition can facilitate the identification of products of processing and prove their naturalness, but is not an objective criterion of specific identification of fruit and berry raw materials.

It follows from the tabular data that fruit and berry raw materials contain such vitamins as B1, B2, B6, PP, β-carotene, K1, E and C. The greatest amount of vitamin C is in wild rose, there are also a lot of group B vitamins in wild rose, tocopherols prevail in wild rose and gooseberry.

Table 4 presents the content of mineral substances in the studied raw materials.

Analyzing Table 4 it is possible to draw a conclusion that all types of fruit and berry raw materials are rich with major macro - and microelements.
Table 1. Carbohydrate composition of fruits and berries, %

<table>
<thead>
<tr>
<th>Type of raw materials</th>
<th>Sugars</th>
<th>Pectic substances</th>
<th>Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Sucrose</td>
<td></td>
</tr>
<tr>
<td>Wild strawberry</td>
<td>3.7–8.1</td>
<td>–</td>
<td>0.7–1.4</td>
</tr>
<tr>
<td>Raspberry</td>
<td>3.6–8.4</td>
<td>0.6</td>
<td>0.5–0.7</td>
</tr>
<tr>
<td>Gooseberry</td>
<td>5.2–13.5</td>
<td>0.3–0.87</td>
<td>3.64–11.0</td>
</tr>
<tr>
<td>Wild rose</td>
<td>8.0–20.0</td>
<td>–</td>
<td>1.8–2.7</td>
</tr>
<tr>
<td>Cherry</td>
<td>6–10.5</td>
<td>0.2–0.31</td>
<td>0.4–0.8</td>
</tr>
<tr>
<td>Bananas</td>
<td>16–19</td>
<td>2.39</td>
<td>–</td>
</tr>
<tr>
<td>Kiwi</td>
<td>7–7.8</td>
<td>0.3–0.5</td>
<td>0.4–0.45</td>
</tr>
</tbody>
</table>

Table 2. Titrable acidity and composition of organic acids

<table>
<thead>
<tr>
<th>Type of raw materials</th>
<th>Titrable acidity, %</th>
<th>Qualitative composition of acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wild strawberry</td>
<td>1.6–2.0</td>
<td>Citric, apple, chlorogenic acids and their derivatives, coumaric, salicylic and cinchonic acid</td>
</tr>
<tr>
<td>Gooseberry</td>
<td>1.5–3.8</td>
<td>Citric, apple, tartaric, succinic and phosphoric acid</td>
</tr>
<tr>
<td>Raspberry</td>
<td>1.3–2.1</td>
<td>Citric, apple, formic, salicylic and chlorogenic acids</td>
</tr>
<tr>
<td>Wild rose</td>
<td>0.9–2.5</td>
<td>Apple acid, phenolic acids</td>
</tr>
<tr>
<td>Cherry</td>
<td>0.5–0.8</td>
<td>Chlorogenic, ellagic, citric, apple, cinchonic, succinic and salicylic acid</td>
</tr>
<tr>
<td>Bananas</td>
<td>0.3–0.4</td>
<td>Apple</td>
</tr>
<tr>
<td>Kiwi</td>
<td>0.6–0.8</td>
<td>Apple, citric, salicylic, chlorogenic acids and their derivatives</td>
</tr>
</tbody>
</table>

Table 3. Content of vitamins in fruits and berries, mg / 100g

<table>
<thead>
<tr>
<th>Type of raw materials</th>
<th>Thiamine (B1)</th>
<th>Riboflavin (B2)</th>
<th>Folic acid (B9)</th>
<th>Niacin (PP)</th>
<th>β-Carotene</th>
<th>Phyllochinone (K3)</th>
<th>Tocopherols (E)</th>
<th>Vitamin C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wild strawberry</td>
<td>0.03</td>
<td>0.05</td>
<td>0.1–0.25</td>
<td>0.3</td>
<td>0.03</td>
<td>0.2–0.4</td>
<td>0.3–0.9</td>
<td>20–55</td>
</tr>
<tr>
<td>Gooseberry</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03–0.26</td>
<td>0.1</td>
<td>0.7–1.0</td>
<td>0.3–1.0</td>
<td>1.0</td>
<td>Up to 110</td>
</tr>
<tr>
<td>Raspberry</td>
<td>0.02</td>
<td>0.05–0.06</td>
<td>0.15–0.32</td>
<td>0.3–0.6</td>
<td>0.2–0.7</td>
<td>0.3–0.6</td>
<td>0.3–0.6</td>
<td>27–93</td>
</tr>
<tr>
<td>Wild rose</td>
<td>0.05</td>
<td>0.3–0.88</td>
<td>0.1–0.25</td>
<td>0.6</td>
<td>2.0–2.6</td>
<td>0.6–1.2</td>
<td>1.0–8.8</td>
<td>670–3800</td>
</tr>
<tr>
<td>Cherry</td>
<td>0.03</td>
<td>0.03</td>
<td>0.05</td>
<td>0.5</td>
<td>0.1</td>
<td>–</td>
<td>0.3</td>
<td>15</td>
</tr>
<tr>
<td>Bananas</td>
<td>0.04</td>
<td>0.05</td>
<td>0.4</td>
<td>0.9</td>
<td>0.12</td>
<td>0.5</td>
<td>0.4</td>
<td>180</td>
</tr>
<tr>
<td>Kiwi</td>
<td>0.02</td>
<td>0.04</td>
<td>0.2</td>
<td>0.5</td>
<td>0.09</td>
<td>–</td>
<td>0.3</td>
<td>180</td>
</tr>
</tbody>
</table>

Table 4. Content of the most important minerals in the composition of fruits and berries, mg/kg

<table>
<thead>
<tr>
<th>Type of berries and fruits</th>
<th>Potassium</th>
<th>Sodium</th>
<th>Calcium</th>
<th>Magnesium</th>
<th>Phosphorus</th>
<th>Iron</th>
<th>Manganese</th>
<th>Cobalt</th>
<th>Molybd-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wild strawberry,</td>
<td>30.8–160</td>
<td>18.0–22.1</td>
<td>27.9</td>
<td>13–18</td>
<td>23–103.6</td>
<td>12.0–103</td>
<td>10–28</td>
<td>0.03–0.052</td>
<td>0.06–0.085</td>
</tr>
<tr>
<td>Gooseberry</td>
<td>260</td>
<td>23</td>
<td>22</td>
<td>9</td>
<td>28</td>
<td>0.8</td>
<td>0.45</td>
<td>–</td>
<td>12 mkg</td>
</tr>
<tr>
<td>Raspberry</td>
<td>24.9–220</td>
<td>23.4</td>
<td>37.1</td>
<td>12.4</td>
<td>37–88.9</td>
<td>16–69</td>
<td>5.2–25.8</td>
<td>0.06</td>
<td>0.004</td>
</tr>
<tr>
<td>Wild rose</td>
<td>23–51</td>
<td>5–6</td>
<td>16–28</td>
<td>6–8</td>
<td>13</td>
<td>24–115</td>
<td>2.2–2.4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cherry</td>
<td>256</td>
<td>20</td>
<td>37</td>
<td>26</td>
<td>30</td>
<td>0.3–0.5</td>
<td>0.08</td>
<td>1 mkg</td>
<td>10 mkg</td>
</tr>
<tr>
<td>Bananas</td>
<td>380–384</td>
<td>28–31</td>
<td>7–8</td>
<td>40–42</td>
<td>26–28</td>
<td>0.6</td>
<td>0.27</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Kiwi</td>
<td>300</td>
<td>5</td>
<td>40</td>
<td>25</td>
<td>30–34</td>
<td>0.6–0.8</td>
<td>0.19–0.21</td>
<td>1.0 mkg</td>
<td>10 mkg</td>
</tr>
</tbody>
</table>
Table 5 gives the indicators of quality. As the tabular data show, the quality of the studied raspberry conforms to the requirements of GOST, the content of toxic elements in raspberry does not exceed the admissible level (Table 12), the samples of raspberries can be applied for further studies.

Table 6 provides data on gooseberry. Analyzing Table 6, it has been established that the samples of gooseberry are typical in shape and coloring, the taste is sourish and sweet, peculiar to this grade, without a foreign smack. The content of toxic elements in gooseberries did not exceed the admissible level (Table 12).

Table 7 provides data on wild strawberry. Proceeding from the data of Table 7, it has been established that the samples of berries of wild strawberry are typical in appearance, coloring, taste and smell, and correspond to the high grade. The content of toxic elements does not exceed the admissible level (Table 12). The berries can be used for further tests.

Table 8 presents the indicators of quality of hips. The tabular data testify that the samples of hips conform to the requirements of GOST for all the indicators and can be used for further tests. The content of toxic elements does not exceed the admissible level (Table 12).

Table 9 gives the indicators of quality of the cherry used for the studies.

Table 5. Indicators of quality of fruits of *Rubus idaeus* (raspberry, the grade “Nagrad”), n = 5

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Characteristics and norms in accordance with GOST</th>
<th>in fact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance, size and structure</td>
<td>Aggregate fruits are rounded or cone-shaped complex stone fruits not stuck together in clumps. Consist of a large number (30–60) of separate, grown together stone fruits. The size of the fruit is from 7.5 to 12 mm. Separate small spherical or ellipse stone fruits, with a stone inside, that has a pitted surface</td>
<td>The fruits are rounded and spherical, not stuck together in clumps. Consist of separate stone fruits grown together (48–60). The size of the fruit is from 9 to 17 mm. Meet the requirements.</td>
</tr>
<tr>
<td>Color of:</td>
<td>Grayish and crimson Pinkish Dark yellow</td>
<td>Crimson red</td>
</tr>
<tr>
<td>surface pulp stones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smell</td>
<td>Specific, pleasant Pleasant, appropriate</td>
<td></td>
</tr>
<tr>
<td>Taste</td>
<td>Sourish and sweet Mainly sweet</td>
<td></td>
</tr>
<tr>
<td>Moisture, %, not more than</td>
<td>15.0</td>
<td>13.0 ± 0.5</td>
</tr>
<tr>
<td>Mass fraction of total ash, %, not more than</td>
<td>3.5</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>Mass fraction of the blackened fruits, %, not more than</td>
<td>8.0</td>
<td>4 ± 0.2</td>
</tr>
<tr>
<td>Mass fraction of the fruits stuck together in clumps, %, not more than</td>
<td>4.0</td>
<td>2 ± 0.5</td>
</tr>
<tr>
<td>Mass fraction of the fruits with unseparated pedicels and receptacles, %, not more than</td>
<td>2.0</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>Mass fraction of the crushed particles of the fruits passing through a sieve with a diameter of openings of 2 mm, %, not more than</td>
<td>4.0</td>
<td>1.5 ± 0.5</td>
</tr>
<tr>
<td>Mass fraction of leaves and parts of raspberry stalks, %, not more than</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Mass fraction of impurities, %, not more than organic (fruits and parts of other nonpoisonous plants)</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>mineral (ground, sand, stones)</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Presence of poisonous plants and their parts</td>
<td>Not allowed</td>
<td>Absent</td>
</tr>
<tr>
<td>Presence of mold and decay</td>
<td>The same</td>
<td>Not detected</td>
</tr>
<tr>
<td>Presence of persistent foreign smell which does not vanish when ventilating</td>
<td>Not allowed</td>
<td>absent</td>
</tr>
</tbody>
</table>
### Table 6. Indicators of quality of fruits of *Ríbesúva-críspa* (garden gooseberry, the grade “Kooperator”), $n = 5$

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Characteristics and norms in accordance with GOST</th>
<th>Characteristics and norms in fact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>The berries are quite developed, healthy, whole, pure, without mechanical damages, the damages caused by depredators and diseases, and excessive external moisture</td>
<td>The berries are mature, healthy, pure, without mechanical damages, depredators and diseases and excessive moisture.</td>
</tr>
<tr>
<td>Coloring</td>
<td>Homogeneous</td>
<td>Homogeneous</td>
</tr>
<tr>
<td>Taste and smell</td>
<td>Peculiar to the given pomological grade, without foreign smell and (or) taste</td>
<td>Sourish and sweet</td>
</tr>
<tr>
<td>Maturity</td>
<td>Harvest</td>
<td></td>
</tr>
<tr>
<td>Content of berries of % of weight, not more than:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanically damaged:</td>
<td>In places of shipment</td>
<td></td>
</tr>
<tr>
<td>At destinations</td>
<td>3.0</td>
<td>1.5 $\pm$ 0.3</td>
</tr>
<tr>
<td>Slightly damaged by powdery mildew</td>
<td>5.0</td>
<td>1.5 $\pm$ 0.2</td>
</tr>
<tr>
<td>Vegetable impurities, % of weight, not more than</td>
<td>Not allowed</td>
<td>absent</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.1 $\pm$ 0.05</td>
</tr>
</tbody>
</table>

### Table 7. Indicators of quality of *Fragaria* (remontant wild strawberry, the grade “Berdskaya rannyaya”), $n = 5$

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Characteristics and norms in accordance with GOST</th>
<th>Characteristics and norms in fact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>The berries are quite developed, healthy, fresh, whole, mature, pure, without mechanical damages and excessive external moisture, with a pedicel or without it, but with a cup. Separate berries without a cup are allowed</td>
<td>The berries are developed, healthy, whole, mature, pure, without mechanical damages and excessive moisture, with a pedicel.</td>
</tr>
<tr>
<td>Taste and smell</td>
<td>Peculiar to the given pomological grade, without foreign smell and (or) taste</td>
<td>Peculiar, without foreign smells and tastes</td>
</tr>
<tr>
<td>Coloring of berries</td>
<td>Homogeneous</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Maturity</td>
<td>The berries are uniform in maturity</td>
<td></td>
</tr>
<tr>
<td>Size to the largest cross-section diameter, mm, not less than:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>for fresh consumption</td>
<td>25.0</td>
<td>$29 \pm 0.5$</td>
</tr>
<tr>
<td>for industrial processing</td>
<td>25.0 (high grade) Not rated (first grade)</td>
<td>–</td>
</tr>
<tr>
<td>Content of berries, % of weight, not more than: mechanically damaged</td>
<td></td>
<td></td>
</tr>
<tr>
<td>in places of shipment</td>
<td>2.0 (high grade) 5.0 (first grade)</td>
<td>$1.0 \pm 0.2$</td>
</tr>
<tr>
<td>at destinations</td>
<td>5.0 (high grade) 10.0 (first grade)</td>
<td>$1.5 \pm 0.5$</td>
</tr>
<tr>
<td>damaged by depredators and birds</td>
<td>2.0 (high grade) 3.0 (first grade)</td>
<td>$1.0 \pm 0.1$</td>
</tr>
</tbody>
</table>
Table 8. Indicators of quality of fruits of *Rosa majalis* Herrm (cinnamon rose), n = 5

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Characteristics and norm for the raw materials used as a medicinal preparation in the food industry as well</th>
<th>in fact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance</strong></td>
<td>The whole false fruits of various shape cleared of sepals and pedicels: from spherical, ovoid or oval to strongly extended spindle-shaped; the length of fruits is 0.7–3 cm, the diameter is 0.6–1.7 cm. There is a small round opening or a pentagonal platform on top of the fruit. Fruits consist of the overgrown receptacle (hypanthium) and numerous fruitlets (nutlets) enclosed in its cavity. The fruit walls are dense, fragile, the external surface is glossy, more rarely mat, more or less savoyed. The fruits are thickly covered inside with long and very stiff bristly hairs. The nutlets are small, oblong, with poorly prominent sides.</td>
<td>Whole, pure, from the spherical to the oval shape, the length of fruits is 1.8–3.2 cm, the diameter is 0.8–1.8 cm. There is a round opening on top of the fruit, the fruits consist of hypanthium and the fruitlets (nutlets) enclosed in its cavity. The walls are dense, the external surface is glossy and savoyed. The fruits are covered inside with long stiff bristly hairs. The nutlets are small, oblong, with poorly prominent sides.</td>
</tr>
<tr>
<td><strong>Color:</strong></td>
<td><strong>fruits</strong> From orange-red to brownish-red</td>
<td>Orange-red</td>
</tr>
<tr>
<td></td>
<td><strong>nutlets</strong> Light yellow, sometimes brownish</td>
<td>Light yellow</td>
</tr>
<tr>
<td><strong>Smell</strong></td>
<td>Peculiar to the given raw materials, without foreign smells</td>
<td>Peculiar, without a foreign smell</td>
</tr>
<tr>
<td><strong>Taste</strong></td>
<td>Sourish and sweet, slightly astringent</td>
<td>Slightly astringent, sourish and sweet</td>
</tr>
<tr>
<td><strong>Moisture, %, not more than</strong></td>
<td>15.0</td>
<td>12 ± 0.5</td>
</tr>
<tr>
<td><strong>Mass fraction of ascorbic acid, %, not less than</strong></td>
<td>0.2</td>
<td>0.4 ± 0.01</td>
</tr>
<tr>
<td><strong>Mass fraction of total ash, %, not more than</strong></td>
<td>3.0</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td><strong>Mass fraction of other parts of the plant (pieces of branches, leaves, sepals and pedicels), %, not more than</strong></td>
<td>2.0</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td><strong>Mass fraction of the blackened and burnt fruits and the fruits damaged by depredators and diseases, %, not more than</strong></td>
<td>1.0</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td><strong>Mass fraction of the crushed particles of fruits, including the nutlets passing through a sieve in accordance with TU 23.2.2068 with the openings with a diameter of 3 mm, %, not more than</strong></td>
<td>3.0</td>
<td>1.0 ± 0.5</td>
</tr>
<tr>
<td><strong>Mass fraction of immature fruits (from the green to yellow coloring), %, not more than</strong></td>
<td>5.0</td>
<td>1.0 ± 0.5</td>
</tr>
<tr>
<td><strong>Mass fraction of impurities: organic (parts of other nonpoisonous plants), %, not more than</strong></td>
<td>0.5</td>
<td>absent</td>
</tr>
<tr>
<td><strong>mineral (ground, sand, stones), %, not more than</strong></td>
<td>0.5</td>
<td>absent</td>
</tr>
</tbody>
</table>
Table 9. Indicators of quality of *Prunus fruticosa* (ground cherry, the grade “Altayskaya lastochka”), n = 5

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Characteristics and norms in accordance with GOST</th>
<th>in fact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>The fruits typical for this pomological grade (first) in shape and coloring. The fruits typical and untypical for this pomological grade (second) in shape and coloring.</td>
<td>The fruits are typical for this pomological grade in shape and coloring.</td>
</tr>
<tr>
<td>Maturity</td>
<td>The fruits uniform in maturity, but not green and not overmature (first grade) The fruits are not uniform in maturity, but not green and not overmature are allowed (second grade)</td>
<td>The fruits are uniform in maturity</td>
</tr>
<tr>
<td>Size to the largest cross-section diameter, mm, not less than:</td>
<td>15 (first grade) Not rated (second)</td>
<td>17 ± 0.5</td>
</tr>
<tr>
<td>including that for small-fruited grades (Vladimirskaya, Samarkandskaya, Rastun’ya, Kartuliaubali, Shubinka) and also that for ground and Nanking cherry</td>
<td>12 (first grade) Not rated (second)</td>
<td>---</td>
</tr>
</tbody>
</table>

Analyzing the data of Table 9, it has been established that the samples of cherry correspond to the first market grade upon the quality indicators, have a typical shape and coloring, the content of toxic elements does not exceed the admissible level (Table 12).

Table 10 gives the indicators of quality of the bananas used for further studies. Mature bananas, i.e. that of the harvest degree of maturity, of extra grade, produced in Ecuador have been studied.

The analysis of tabular data testifies that the samples of bananas correspond to the market extra grade, the content of toxic elements does not exceed the admissible level (Table 12).

Table 11 presents the indicators of quality of the studied fruits of kiwi.

It follows from the tabular data that the samples of kiwi are high-grade and can be used for further studies. The content of toxic elements does not exceed the admissible level (Table 12).

The analysis of tabular data testifies that the quality of the studied types of fruit and berry raw materials conforms to the requirements of normative documents according to the content of toxic elements and can be applied for further tests and the determination of specific identification.

The performed assessment of quality of fruit and berry raw materials with the application of organoleptic and physical and chemical methods of analysis provided by the existing normative documents has shown that the organoleptic method of assessment is the most acceptable for the purpose of identification of fresh fruits and berries. In case of the processed raw materials this method is subjective and is based only on the definition of taste, aroma and color of the applied vegetable raw materials which can be imitated by means of nutritional supplements - dyes and fragrances [14].

The physical and chemical indicators, such as the content of solids, sugars, pectinaceous substances, organic acids and titrable acidity can not be the objective criteria of identification of the crude and processed fruit and berry raw materials as their values are very close, and sometimes coincide in different types of raw materials. Some indicators, such as the content of vitamin C and total of carotinoids can indirectly be suitable for the identification of group of fruit and berry raw materials, but they do not allow to define a type of fruit and berry raw materials [15, 16].

Some physical and chemical methods, for example IR-spectrometry, allows to identify fresh fruit and berry raw materials and to establish the fact of availability of fruit and berry raw materials in foodstuffs, but does not allow to reveal their species [17].

Thus, the performed studies on the assessment of quality of the fresh and processed fruit and berry raw materials have shown that the organoleptic and physical and chemical methods of analysis regulated by the existing regulatory system have limited capacities in the assessment of species of raw materials.
Table 10. Indicators of quality of *Musa paradisiaca* (banana of "Extra" grade), n = 5

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Characteristics and norm for the grades</th>
<th>in fact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance</strong></td>
<td>The fruits are of the same pomological grade. The fruits in brushes are dense, fresh, pure, whole, healthy, developed, not miss-shaped, without flower remains, with highly prominent ridge sides. The crown is green, its cutoffs are plain, smooth, healthy, not overdried</td>
<td>The fruits are of the same pomological grade. The fruits in brushes are dense, fresh, pure, whole, healthy, with highly prominent ridge sides. The crowns are green, their cutoffs are plain, smooth, not overdried</td>
</tr>
<tr>
<td><strong>Taste and smell</strong></td>
<td>A specific smell of ripe bananas, the taste is sweet, without a foreign smack and aroma</td>
<td>The taste is specific, sweet, without a foreign smack and aroma</td>
</tr>
<tr>
<td><strong>Maturity</strong></td>
<td>When cutting fruits lacteal juice is well emitted. The fruits are of the harvest degree of maturity with a greenish-yellow or yellow skin but not overmature, dense, roundish, the pulp is creamy</td>
<td>When cutting fruits lacteal juice is well emitted. The fruits are of the harvest degree of maturity with a yellow skin, not overmature, dense, roundish, the pulp is creamy</td>
</tr>
</tbody>
</table>

Sizes of the fruits:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>to the largest cross-section diameter, cm</td>
<td>3.0–4.0</td>
<td>3.0 ± 0.3</td>
</tr>
<tr>
<td>in length, cm, not less than</td>
<td>20.0</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td>21.0 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>Quantity of fruits in a brush, pcs.</td>
<td>4–8</td>
<td>4–9</td>
</tr>
<tr>
<td></td>
<td>7 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>Quantity of brushes per one packing unit, pcs.</td>
<td>15–18</td>
<td>14–18</td>
</tr>
<tr>
<td></td>
<td>17 ± 0.9</td>
<td></td>
</tr>
</tbody>
</table>

Content of bananas with deviations from the fixed sizes of no more than:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>to diameter by 0.5 cm, %, not more than</td>
<td>2.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>1.0 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>in length by 1.0 cm, %, not more than</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>2.0 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>The surface damages of skin without touching the pulp, mechanical damages and those caused by agricultural depredators on one fruit with the total area of, cm², not more than</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0.5 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

Content of fruits with latex streaks (spots), %, not more than:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>- in area not more than 10 cm²</td>
<td>Not limited</td>
<td>0</td>
</tr>
<tr>
<td>- in area more than 10 cm²</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Content of the broken fruits, with a tear of skin at the pedicel, with deep cuts, strong pressings, skin cracks when the pulp is touched, affected with anthracnose, fusariosis, Sigatoka disease, decayed, rotten, soften, chilled to the 3-4th degree, frozen, mashed, with extensive damages caused by agricultural depredators (skin plagues, deep red spots of nesting of trips), overmature with a dark brown, black or spotty skin

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not allowed</td>
<td>absent</td>
</tr>
</tbody>
</table>
Table 11. **Beginning.** Indicators of quality of fruits of *Actinidia delicosa* (kiwi delicious), \( n = 5 \)

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Characteristics and norm for the market grades</th>
<th>in fact</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>high</td>
<td>first</td>
</tr>
<tr>
<td>Appearance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slight surface defects of skin which do not affect the quality are allowed</td>
<td>Fruits with slight deficiencies in shape, but without outgrowths and deformations, slight coloring defects, slight skin defects the total area of which does not exceed 1 cm, with small traces from the removed label in the form of longitudinal lines, without hillocks are allowed</td>
<td>Deficiencies in shape, coloring, skin defects in the form of slight cicatrized cracks or scratched/torn off skin the total area of which does not exceed 2 cm, with more prominent traces from the removed label, with small hillocks and slight dents are allowed</td>
</tr>
<tr>
<td>Appearance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smell and taste</td>
<td>Peculiar to the given pomological grade, without a foreign smell and taste</td>
<td>peculiar, without foreign</td>
</tr>
<tr>
<td>Internal structure</td>
<td>The pulp is dense, juicy and tough, without damages</td>
<td>The pulp is dense, juicy and tough, without damages</td>
</tr>
<tr>
<td>The ratio of the minimum diameter to the maximum diameter of the fruit measured in cross section, not less than</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Mass of fruits, not less than</td>
<td>90.0</td>
<td>70.0</td>
</tr>
<tr>
<td>Maturity degree</td>
<td>Homogeneous</td>
<td>Homogeneous</td>
</tr>
<tr>
<td>Mass fraction of soluble solids, %, not less than</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>Mass fraction of the fruits with deviations of more than 10% from the fixed weight, % of weight, not more than</td>
<td>Not allowed</td>
<td>5.0</td>
</tr>
<tr>
<td>Mass fraction of the fruits with slight deficiencies in shape and coloring, with slight dents, with small hillocks, %, not more than</td>
<td>Not allowed</td>
<td>5.0</td>
</tr>
<tr>
<td>Mass fraction of the fruits with surface skin defects, the total area of which is not more than 1 cm, %, not more than</td>
<td>Not allowed</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Table 11. Ending. Indicators of quality of fruits of *Actinidia deliciosa* (kiwi delicious), n = 5

<table>
<thead>
<tr>
<th>Name of the indicator</th>
<th>Characteristics and norm for the market grades</th>
<th>in fact</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>high</td>
<td>first</td>
</tr>
<tr>
<td>Mass fraction of the fruits with skin defects in the form of cicatrized cracks or scratched/torn off skin, the total area of which is not more than 2 cm, %, not more than</td>
<td>Not allowed</td>
<td>Not allowed</td>
</tr>
<tr>
<td>Mass fraction of the faded, mushy, watery, overmature, moldy and decayed fruits and the fruits damaged by insect depredators, with mechanical damages, with the damaged pulp, with excessive external moisture, %, not more than</td>
<td>Not allowed</td>
<td></td>
</tr>
<tr>
<td>Mass fraction of the fruits grown together, %, not more than</td>
<td>Not allowed</td>
<td></td>
</tr>
</tbody>
</table>

Table 12. Content of toxic elements in berries and fruits

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Name of the element</th>
<th>plumbum</th>
<th>arsenic</th>
<th>cadmium</th>
<th>mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raspberry</td>
<td>0.023</td>
<td>less than 0.02</td>
<td>0.011</td>
<td>less than 0.00002</td>
<td></td>
</tr>
<tr>
<td>Gooseberry</td>
<td>0.029</td>
<td>less than 0.02</td>
<td>0.012</td>
<td>less than 0.00002</td>
<td></td>
</tr>
<tr>
<td>Wild strawberry</td>
<td>0.030</td>
<td>less than 0.02</td>
<td>0.013</td>
<td>less than 0.00002</td>
<td></td>
</tr>
<tr>
<td>Cherry</td>
<td>0.075</td>
<td>less than 0.04</td>
<td>less than 0.01</td>
<td>less than 0.00002</td>
<td></td>
</tr>
<tr>
<td>Wild rose</td>
<td>0.040</td>
<td>less than 0.04</td>
<td>less than 0.01</td>
<td>less than 0.00002</td>
<td></td>
</tr>
<tr>
<td>Bananas</td>
<td>0.030</td>
<td>less than 0.03</td>
<td>less than 0.005</td>
<td>less than 0.00002</td>
<td></td>
</tr>
<tr>
<td>Kiwi</td>
<td>0.030</td>
<td>less than 0.03</td>
<td>less than 0.005</td>
<td>less than 0.00002</td>
<td></td>
</tr>
<tr>
<td>Dichlorophenoxyacetic acid, mg/kg in accordance with SanPiN 2.3.2.1078-01</td>
<td>max. 0.4</td>
<td>max. 0.2</td>
<td>max. 0.03</td>
<td>max. 0.02</td>
<td></td>
</tr>
</tbody>
</table>

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Abstract: The main problem of implementation of technology of rutin extraction from grass buckwheat Fagopyrum sagittatum Gilib. lies in purification of rutin raw. In this connection the following research object is determined: consideration of the possibility to use for rutin raw purification different commercial carbon brands as adsorbents by the method of preparative chromatography and assessment of their effectiveness to achieve the maximum degree of purification with minimum duration of the elution process. The article presents experimental data on purification of rutin raw sample, extracted from grass buckwheat green material by the preparative chromatography method using wood- and coconut-based activated carbons of different brands as sorbents; besides, the following items are presented in the article: dependence of rutin sample melting temperature, qualitative and quantitative flavonoid content, authenticity on chlorophyll and red pigments content depending on sorbent layer height and elution duration in comparison with the GSO [State Standard Samples] control sample. To confirm the reliability of the obtained results, statistical processing of experimental data is conducted using the methods of correlation and regression analysis, as well as using the two-parameter normal distribution of values. It is demonstrated that the use of the following carbon brands, indicated in decreasing effectiveness order, can provide the best purity and stability of parameters values, characterizing the product: NWC-P, NWM-P, OU-A, OU-B; the conducted calculations indicate that the best correlation between the sorbent layer height in a column and the rutin samples quality parameter was achieved when the carbons of the brands NWM-P, OY-A and OY-B were used. Depending on the tasks, rutin purification degree may be regulated by sequential use of NWC-P and NWM-P carbons. When rutin is purified from proximate admixtures, chlorophyll and red pigments, NWC-P adsorbent allows to get a comparable result even when the layer height is from 50 to 70 mm respectively.

Keywords: Grass buckwheat, rutin raw, activated carbon, purification, method of preparative chromatography

INTRODUCTION

Nowadays, a special place in the pharmaceutical market is occupied by medicines and dietary supplements of plant origin, containing flavonoids, one of the most important qualities of which is the ability to increase strength of the capillary walls. P-vitamin activity of these medicines is associated with the antioxidant effect that is important in the treatment of chronic venous insufficiency, hypertension and other cardiovascular diseases, associated with the increased permeability of blood capillaries. The closest representative of this group of substances is rutin, which not only has a pronounced capillary-strengthening, antioxidant and hepatoprotective action [1, 2], but also improves the treatment of various disorders, associated with physical fatigue [3].

Today the main industrial source of rutin is the buds of Japanese pagoda tree (Styphnolobium japonicum L.), however, there is no raw material base of this plant in our country. A promising domestic source of rutin and other flavonoids may be grass buckwheat (Fagopyrum sagittatum Gilib.), widely cultivated as a valuable food crop in the Russian Federation. It is known that the rutin content in the cultivated buckwheat sorts is from 2.0 to 8.7% on a dry basis. However, the sorts, the rutin content in which may be 12%, are selected [4, 5].

Despite the broad prospects of the use of grass buckwheat as a raw material for the rutin production, the main difficulty of the implementation of technology of rutin extraction lies in the stage of rutin raw purification and obtaining a product, suitable for use in pharmaceutical industry and dietary supplements production [6]. In view of this, studies have been conducted on the use of commercial carbons of different brands as adsorbents, used for rutin purification, by the method of preparative chromatography, as well as the assessment of their effectiveness to achieve the maximum degree of purification with minimum duration of the elution process was conducted.
OBJECTS AND METHODS OF STUDY

The study objects were rutin raw samples, extracted by the above-mentioned method [7, 8] and purified by the method of preparative chromatography on a layer of wood- and coconut-based activated carbon of six brands. Physical and chemical parameters of the carbons are indicated in Table 1.

Sample melting temperature was measured with the device PTP (M), qualitative and quantitative flavonoid content in the samples was measured by the method of HPLC on high performance liquid chromatograph Milikhrom A-02 with UV radiation and a chromatographic column from stainless steel activated carbons of different brands, the rutin samples of the sample of purified rutin.

Produced at a speed of 1 drop in a second. Sorbent of the prepared sorbent layer, eluent feed to the column is of 15 mm activated carbon is placed (layer height is 360 mm and diameter of 2775 mm, filled with a reversed-phase sorbent ProntoSIL 120-5C18 AQ, with a software package. The solution of 0.1% acetic acid and acetonitrile was used as an eluent. Flavonoid retention time is 25 minutes. Chlorophyll and red pigments content was measured by spectrometric method. The readings were taken from the devices Shimadzu UV-2401 PC UV-VIS RECORDIGPHOTOMETER (Japan) at wave length of 560 nm, 590 nm, 620 nm, 655 nm and 690 nm in a cuvette with the layer thickness of 1 cm. Isopropyl alcohol was used as a comparison solution. Microscopic examination of rutin samples was conducted with the electron microscope SK 14 28804.

Table 1. Physical and chemical parameters of activated carbons of different brands [9]

<table>
<thead>
<tr>
<th>Carbon brands</th>
<th>Appearance</th>
<th>Adsorption activity by methylene blue, mg/g</th>
<th>Ash mass fraction, %</th>
<th>Moisture mass fraction, %</th>
<th>Bulk density, g/dm³</th>
<th>Abrasion capacity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>OU-A (GOST 4453-74)</td>
<td>Black fine-grained powder</td>
<td>225.0</td>
<td>4.6</td>
<td>4.7</td>
<td>270</td>
<td>60</td>
</tr>
<tr>
<td>OU-B (GOST 4453-74)</td>
<td>Black fine-grained powder</td>
<td>75.0</td>
<td>10.0</td>
<td>10.0</td>
<td>290</td>
<td>60</td>
</tr>
<tr>
<td>BAU-A (GOST 6217-74)</td>
<td>Black grains</td>
<td>60.0</td>
<td>6.0</td>
<td>10.0</td>
<td>240</td>
<td>60</td>
</tr>
<tr>
<td>BAU-MF (GOST 6217-74)</td>
<td>Black grains</td>
<td>70.0</td>
<td>10.0</td>
<td>10.0</td>
<td>Not regulated</td>
<td>60</td>
</tr>
<tr>
<td>NWC-P, FCC specification</td>
<td>Black powder</td>
<td>300.0</td>
<td>5.0</td>
<td>15.0</td>
<td>300</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>NWM-P, FCC specification</td>
<td>Black powder</td>
<td>280.0</td>
<td>10.0</td>
<td>15.0</td>
<td>300</td>
<td>&gt; 96</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Rutin raw was extracted from grass buckweat green material by double extraction with ethanol solution of 70%. The output was 4.44 ± 0.05% (on absolute dry substance), contain of main substance in a sample was 75.74%, melting point was 162°C, crystals were gray-and-green. According to regulating documentation requirements, the rutin content shall be at least 95.0% (State Pharmacopoeia XI); in the GSO [State Standard Sample] sample it was at least 98.5%. For purification of rutin raw we offered the method of preparative chromatography on a layer of activated carbons of different brands – OU-A, OU-B, BAU-A, BAU-MF, NWC-P, NWM-P [10]. 99.5%-methanol was used as a solvent and eluent for chromatography.

In a column with a height of 360 mm and diameter of 15 mm activated carbon is placed (layer height is from 10 to 100 mm). Rutin raw solution is applied to the prepared sorbent layer, eluent feed to the column is produced at a speed of 1 drop in a second. Sorbent layer height in a column corresponds with the number of the sample of purified rutin.

After rutin raw purification with the use of activated carbons of different brands, the rutin samples were analyzed for compliance with the melting temperature, the content of flavonoids and authenticity in the presence of chlorophyll and red pigments in comparison with the GSO [State Standard Samples] control sample. All the used brands of carbons are activated and represented in 87–97 mas.% of composition of elements by carbon. The main structural element of the activated carbon sorption space at the organization molecular level is the graphite basal face, which is formed by carbon atoms in the state of sp²-hybridization with delocalized fourth electron. Non-specific physical adsorption is realised on them by means of universal forces of dispersion interaction. Besides, non-specific electrostatic induction forces are expressed in carbon like in conductor by means of dipole direction in the sorbate molecule. Their intensity is determined by polarization capacity. Carbons express capacity to sorption by means of addition of these forces. At the same time, oxigenated functional groups and Bronsted acids are present on the surface initially and appear during activation process by overheated moisture vapour. They are represented by hydroxyl, phenol, carboxyl, carbonyl and lactone groupings, content and balance of which are different for different carbon brands [11]. It should be noted that acidic properties of the carbon surface change in the following sequence: NWM-P<NWC-P<OU-A, OU-B<BAU-MF<BAU-A. In other words, on the surface of NWM-P carbon there is minimum number of acidic groups from all the materials under consideration, and on the surface of BAU-A carbon this number is maximum. NWM-P and
NWC-P carbons express high reducing ability in comparison with BAU and OU carbons.

The research results of melting temperature determination are indicated in Fig. 1–3. According to the obtained dependences of Fig. 1, one can achieve the rutin highest melting temperature, which is one of the product characteristics, using NWC-P, NWM-P and OU-B carbons. Moreover, only when these brands of adsorbents are used, there is a dynamic in a positive index changing with carbon layer increase in a column. Rutin samples, purified on NWC-P carbon layer, are the closest to the control sample.

Processing of experimental data results on rutin raw purification with the use of the normal distribution is indicated in Fig. 2.

---

Fig. 1. Dependence of rutin samples melting temperature on carbon brand.

Fig. 2. Normal distribution of melting temperature values of rutin samples depending on carbon brand.
According to Fig. 2, the adsorbent efficiency of BAU-A and OU-A carbons nearly does not depend on the layer height in a column. Herewith, the use of OU-A carbon allows to get a stable result of melting temperature of 181.9°C with narrow distribution. BAU-MF adsorbent is absolutely ineffective, having wide distribution with an average value of 165.4°C. NWM-P and NWC-P adsorbents, having wide distribution, allow to get an average result of 183.3°C and 186.1°C respectively. Maximum purification degree for the carbons of these brands is determined by a much higher specific surface (1.5–2.0 times higher) in comparison with wood-based activated carbon. Coconut-based carbons are sorbents with pores of mixed type with nearly equal volume of micro- and mesopores, whereas wood-based activated carbons are characterized by a large proportion of macropores, acting as transporting channels which bring adsorbate molecules to adsorption space of the activated carbon particles. In this regard, wood-based adsorbents purification efficiency is directly connected with the layer height, it is expressed especially clearly in OU-V activated carbon which has the widest distribution.

Dependence of the use of the studied activated carbon brands on the layer height in a column concerning the melting temperature changing of rutin samples is indicated in Fig. 3.

The calculation results indicate that the highest correlation between the layer height and the achieved result is observed in NWM-P, OU-B and BAU-MF adsorbent brands with a direct correlation coefficient $r = 0.9601$, $r = 0.9265$ and $r = 0.9159$ respectively. Direct correlation coefficient value more that 0.75 indicates strong dependence between the layer height changing and the result obtained. Thereunder, when OU-A carbon is used for rutin raw purification, the results strongly depend on the layer height ($r = 0.7381$).

Qualitative and quantitative flavonoid contents in the rutin samples were defined with thin-layer chromatography (TLC) and high-efficiency liquid chromatography (HELC) methods. According to TLC, rutin raw contains a foreign admixture - quercitin, which is removed due to purification with the use of NWC-P and OU-B carbons regardless the sorbent layer height. The same effect can be achieved using OU-A and NWM-P carbons with the layer height in a column more than 40 mm. HELC analysis results are indicated in Fig. 4–6.

According to the data of Fig. 4, the greatest purification of the product can be achieved using NWC-P and NWM-P adsorbents. Moreover, only for these activated carbon brands there are stable positive dynamics of admixture reduction when the adsorbent layer in a column increases. However, rutin samples purified with NWC-P carbon, are the closest to the control sample in their parameters.

![Fig. 3. Dependence of rutin melting temperature on adsorbent layer height.](image-url)
Processing of experimental data results on rutin raw purification with the method of normal distribution (Fig. 5) showed that the efficiency of BAU-A and OU-A adsorbents nearly does not depend on the layer height in a column. Herewith, use of OU-A carbon allows to get a stable result of 82.6% with narrow distribution. BAU-MF adsorbent is absolutely ineffective, having wide distribution with an average value of 73.8%, and NWM-P and NWC-P adsorbents, having the widest distribution, allow to get an average result of 86.9% and 92.3% respectively.

Dependence of the carbon brand efficiency on the layer height in a column is indicated in Fig. 6. The calculation results indicate that the highest correlation between the layer height and the achieved result is observed in NWM-P and OU-B adsorbent brands with correlation coefficients \( r = 0.9170 \) and \( r = 0.8940 \) respectively, for BAU-MF and NWC-P activated carbons correlation is less expressed with coefficients \( r = 0.7142 \) and \( r = 0.7235 \) respectively. Direct correlation coefficient value more that 0.75 indicates strong dependence between the layer height changing and the result obtained. If OU-A activated carbon is used as an adsorbent, there is no correlation among the studied parameters \( (r = 0.0579) \). Sorption rutin extraction is far less in comparison with its aglycone—quercetin, which may be connected with different adsorption nature, especially with the structure and the data size of polyphenol molecules. Functional groups on the activated carbon surface interact with phenol compounds due to Van der Waals forces in micropores and hydrogen bonds appearance in mesopores, herewith, the bigger and more polar glycoside molecule is adsorbed slower. Taking into account sub-acid nature of the split flavonoids, adsorption activity of the carbons, used in the present research, will be changed in a sequence, contrary to the surface acidic properties changing.

According to the results, obtained by mathematic treatment of experiments on determination of mass fraction of flavonoid amount, it can be stated that purification has a positive effect on the main substance content, extracted after the use of NWC-P and NWM-P carbons.

Rutin authenticity is confirmed by the results of determination of chlorophyll and red pigments content and is indicated in Fig. 7-9.

The obtained dependences of Fig. 7 show that the use of NWC-P, BAU-MF and BAU-A adsorbents allows to achieve the lowest chlorophyll and red pigments content, whereas using NWM-P carbon, a substantial increase in chlorophyll and red pigments content is observed.

Processing of experimental data results on rutin raw purification with the method of preparative chromatography with the use of normal distribution is indicated in Fig. 8.

According to Fig. 8, the efficiency of BAU-A and BAU-MF carbons nearly does not depend on the layer height in a column and allows to get a stable result of 0.00016% with narrow distribution. NWM-P carbon is absolutely ineffective in this case, having wide distribution with an average value of 0.00056%. It may be connected with the pore structure of the adsorbents under consideration: micropores, presence of which is typical for coconut-based carbons, are especially
suitable for adsorption of small molecules, whereas chlorophyll and red pigments are of quite big sizes. In this case, polymolecular adsorption is most effective which takes place in mesopores at sequential appearance of adsorption layers and which ends with pore filling by a mechanism of capillary condensation.

**Fig. 5.** Normal distribution of flavonoid amount content values in rutin samples depending on carbon brand.
Layer height, mm: NWC-P: $r = 0.7235; y = 86.2166667 + 0.110842424 \cdot x$

**Fig. 6.** Dependence of flavonoid amount content in rutin samples on adsorbent layer height.

![Graph showing flavonoid amount content vs. adsorbent layer height](image)

**Fig. 7.** Dependence of chlorophyll and red pigments content in rutin samples on carbon brand.

![Graph showing chlorophyll and red pigments content vs. carbon brand](image)
Dependence of the carbon brand efficiency on the layer height in a column is indicated in Fig. 9. The calculation results indicate that the highest correlation between the layer height and the achieved result is observed in OU-A, NWM-P and OU-B adsorbent brands with an invert correlation coefficient \( r = -0.9707 \), \( r = -0.9359 \) and \( r = -0.9359 \) respectively. OU-A and OU-B adsorbents are brightening carbons with mesopore volume of 0.7 cm\(^3\)/g and specific surface of 200–450 m\(^2\)/g, in contrast to other brands of activated carbons, for which these indexes are much lower and are 0.002–0.10 cm\(^3\)/g and 20–70 m\(^2\)/g respectively. According to the analysis of the obtained data, authenticity of all tested rutin samples is confirmed, which indicates strong correlation between the parameters under study and the adsorbent brand.

Thus, the use of the following carbon brands, indicated in decreasing effectiveness order, can provide the best purity and stability of parameters values, characterizing the product: NWC-P, NWM-P, OU-A and OU-B, excluding the authenticity index, where NWM-P carbon had the worst result.

The best correlation between the layer height in a column and product quality parameter was achieved, when NWM-P, OU-A and OU-B carbons were used, excluding the experiment on flavonoid amount content, where OU-A carbon showed no dependence.

Depending on the tasks, rutin purification degree may be regulated by sequential use of NWC-P and NWM-P carbons. Moreover, when rutin is purified from proximate admixtures, chlorophyll and red pigments, NWC-P adsorbent allows to get a comparable result even when the layer height is from 50 to 70 mm respectively. These data are proved by rutin samples micro-copying. After purification with NWC-P carbon, the crystal form is needle-like, identical to the GSO [State Standard Samples] control sample, which characterizes substance high purity. These data are indicated in Table 2.

Based on the results of Table 2, it should be noted that physical and chemical properties of the studied rutin samples No. 5 and No. 7 comply with State Pharmacopoeia XI after purification.
Table 2. Rutin physical and chemical parameters

<table>
<thead>
<tr>
<th>Rutin sample</th>
<th>Crystals colour</th>
<th>Melting temperature, °C</th>
<th>Crystals form</th>
<th>Crystals size, µm</th>
<th>Rutin content, %</th>
<th>Flavonoids, different from rutin * (TLC data)</th>
<th>Ultraviolet spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSO</td>
<td>yellow-green</td>
<td>190</td>
<td>needle-like</td>
<td>0.33–153.30</td>
<td>98.56</td>
<td>1; 2</td>
<td>258.0 361.0</td>
</tr>
<tr>
<td>Rutin raw</td>
<td>greyish-green</td>
<td>162</td>
<td>irregular</td>
<td>1.66–203.13</td>
<td>75.74</td>
<td>1; 2 3</td>
<td>258.0 361.0</td>
</tr>
<tr>
<td>Sample No. 5</td>
<td>yellow with the greenish cast</td>
<td>189</td>
<td>needle-like</td>
<td>0.42–159.00</td>
<td>96.25</td>
<td>1; 2</td>
<td>257.0 361.0</td>
</tr>
<tr>
<td>Sample No. 7</td>
<td>yellow with the greenish cast</td>
<td>189</td>
<td>needle-like</td>
<td>0.66–153.15</td>
<td>97.88</td>
<td>1; 2</td>
<td>258.0 361.0</td>
</tr>
</tbody>
</table>

Notes. * 1 - kaempferol-3-O-rhamnoside; 2 - isoquercitrin; 3 – quercitrin.

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FISCAL TECHNOLOGIES OF BUDGET LIQUIDITY MANAGEMENT AND THEIR ROLE TO ENSURE THE SUSTAINABLE GROWTH OF THE AGRARIAN SECTOR IN THE CONTEXT OF GLOBAL UNCERTAINTY

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Abstract: When the political and economic uncertainty rises, the sustainable functioning of strategically significant industries that first and foremost include the agriculture defines the national security. Comparison of the agricultural output in Russia and some global countries indicate on extensive pattern of the growth in industry. The government too poorly commits to support the agricultural sector. Where the budget revenue declines in the Russian Federation due to unfavorable conditions in the commodity markets, the risks of non compliance with expenditure commitments increase (in particular, program events focused on the agrarian sector support). The purpose of the study was to justify the feasibility to increase the share of government in the activity to ensure the growth of the industry at the brand-new level by using up-to-date fiscal technologies for budget liquidity management. The study was based on the dialectical approach that allows considering components (elements) of the agrarian sector in their flow and development along with systematic and institutional methodological approaches and statistical methods. Fiscal technologies for budget liquidity management are aimed at reducing budgetary risks that arise when implementing budget plans under conditions of global uncertainty. Concentration of financial assets with the Unified Bank Account of the Treasury of Russia and placement of temporarily free budget liquidity in derivative instruments forms conditions to create the innovative and investment-oriented budget deficit and increase of the governmental share in development of the industry at the truly new level.

Keywords: Agriculture, agrarian sector, sustained development, food security, targeting of budget funds remainders, liquidity of the single budget account, budgetary risks, budget data, innovation and investment-oriented budget deficit


INTRODUCTION

Sustainability of the agricultural sector is one of strategic priorities that specify the national food security. It is obvious that the food security development greatly relates to the matter of programs and policies integrated at the national level, oriented to creation of the environment convenient for business and growth of agricultural output.

For 26 years, quite a long period in history, when Russia was undergoing formation and development of market relations, a range of legislative and regulatory laws were adopted along with documents of state strategic planning system \textsuperscript{1} (forecasts, concepts, strategies, programs, activity plans, etc.) to show the opinion and intentions of federal and regional authorities towards agricultural activity, the industry so significant to ensure the national security. Its significance for the national economy is evident from that the term "agriculture" is mentioned 7669 times in the text of the Russian legislation, and 1200 to 8000 more times in the legislation of the constituent entities.

It is necessary to point out that in the Russian Federation institutional frameworks are mainly formed aimed to ensure the governmental support to agricultural sector.

The Concept of Long-Term Social and Economic Development of the Russian Federation for the period up to 2020 [1], as well as the Food Security Doctrine of the Russian Federation serve as the key instrument that

\textsuperscript{1} The documentation system of state strategic planning is defined in the Art. 3 of the Federal Law 3 No. 172-FZ "On Strategic Planning in the Russian Federation" dated June 28, 2014.
specify major objectives of the governmental agrarian policy for strategic outlook [2]. In December 2010, the Concept of Sustainable Development of Rural Territories of the Russian Federation for the period to 2020 was approved [3], and the Strategy for Agricultural Machinery Development in Russia for the period to 2020 [4] was approved in December 2011.

The Art. 6 of the Federal Law "On Agriculture Development" [5] specifies measures to implement the governmental agrarian policy, including the budgetary funds granted to agricultural producers, and the Art. 7 of the same specifies main areas of public support to this industry. In particular, this includes availability of credit resources for agricultural producers, provided that the share of sale revenue of agricultural products is at least 70% per calendar year of the total income of the entity; development of the risk insurance system in agriculture, of livestock breeding, elite seed production, and others. (sub-clause 1, cl. 1, Art. 7). The federal budget fund is the source of finding of such activities granted as budget subsidies to budgets of the RF constituent entities as prescribed by the Government of the Russian Federation.

In 2007, the State Program for Agriculture Development and Regulation of Agricultural Products, Raw Material and Foodstuff Market for 2008–2012 was adopted [6]. As the list of the RF state programs [7] is approved to integrate the program-targeted principles of budget planning, the program matter was updated, and the timeline was extended to 2020 [8].

Initially, in 2008-2012, the program was assumed to be implemented based on co-financing at the expense of assets as follow: 551.3 billion rubles (39.2%) – federal budget assets; 544.3 billion rubles (38.7%) – budget assets owned by RF entities; 311 billion rubles (22.1%) – extrabudgetary sources, and the total scope of finance under the program amounted to 1406.6 billion rubles. However, the program funding sources were revised. To implement the program within 2013–2020, the federal budget funds were assumed only in the amount of 2126.2 billion rubles (that is, 3.8 times higher compared to the amount scope of budget allocations under the federal budget for 2008–2012).

It should be noted that the RF constituent entities also adopted state programs aimed at support to the agrobusiness. The presence of regions in this process is obviously defined by budget capacity of thereof.

The overarching policy of the Russian Federation to take part in the international agriculture, fisheries and food security activity [9] specifies that the sustainable and predictable development of agriculture is becoming more urgent against the world crises, including food and financial sectors that managed to radically transform the condition related to ensure the food security in Russia in recent days.

The political events of 2014–2016 (the Ukrainian crisis followed by annexation of the Crimea to the Russian Federation, the presence of the National Guard troops in Syria, etc.) fatally resulted in the growth of global political and economic uncertainty. Economic sanctions against Russia by the United States and the European Union countries, the restriction or embargo on the supply of certain food and the similar triggered actions by the President of the Russian Federation and the Government of the Russian Federation to focus on sustainable development of agriculture for the purpose to introduce the policy of import substitution and ensure the national food security.

As the response to economic sanctions by the West, on January 1, 2015, the President of the Russian Federation caused the formation of the Eurasian Economic Union (EEU) with Belarus, Kazakhstan, Armenia as members and Kyrgyzstan that joined them six months later. The purpose of EEU is to ensure the free flow of goods, services, capital assets, labor and introduction of the well-coordinated, consistent or unified policy for economic sectors, including agriculture. The intentions of various countries (Egypt, Thailand, Iran, Mongolia, Serbia) to join the EEU prove their concern.

The purpose of this study is to provide evidence on feasibility to increase the governmental share to ensure the game-changing industrial development through the employment of recent fiscal technologies to manage the budget liquidity based on assessment results for the Russian agrarian sector condition and comparison data of industrial performance between some countries of the world, the development level of institutional environment oriented to the agriculture support, as well as based on the volume of budgetary resources available in the pre-crisis period and in the midst of increasing global uncertainty.

OBJECTS AND METHODS OF STUDY

The target of research is the agrarian sector with reference to processes that characterize its capacity against the growing budget constraints related to fiscal technologies of public liquidity management and the share of such technologies in the sustainable development of the industry to the brand-new level. The research is based on the dialectic approach. In the course of the research, systematic, institutional methodological approaches and statistical methods were applied.

The dialectical approach allows to study agrarian components (elements) on the movement and in process. In turn, the system concept allows assessing the impact of the agrarian sector pattern, as a subsystem, on the supersystem stability that is the national economy as a whole, and considering the interaction between these different systems. The use of the system concept affords to analyze the interaction of the agrarian sector as a national economy subsystem with other subsystems, for instance, with the government sector. The institutional approach is focused on the study of the agrarian sector in terms of assessment of the health, level and directions of the institutional environment development, including such institution as the Federal Treasury and technologies used by thereof to manage budget liquidity.

The analysis of statistical time series makes it possible to track the industrial changes in correlation with a variety of macroeconomic parameters, for example, incomes and expenditures of the consolidated
RESULTS AND DISCUSSION

The comparative analysis and the assessment of the agricultural sector capacity in relation to some macroeconomic parameters

Gross Regional Product (GRP) serves as the summarized performance measure of the state-of-the-art of regional economy and the significance of certain types of economic activity in formation thereof. The analysis of the GRP structure for Russian regions showed that only 21 out of 85 RF entities significantly contribute to ensure the national food security with over 10% share of such business activities as "Agriculture, hunting and fishing" (Fig. 1). If the share of the industry in the GRP structure is taken as 15% and over as the estimation criterion, there are only 11 regions in the Russian Federation with such parameters (Fig. 1). Among them, the Republic of Kalmykia (31.3%), Belgorod (20.3%), Kursk (18.1%), Orel (16.8%), Tambov (21.9%), Stavropol Territory (15.0%), Kabardino-Balkar Republic (16.2%), Karachay-Cherkess Republic (19.2%), and Mariy-Eli (18.0%), Altai (18.3%) and the Crimea (21.9%) [10].

Moreover, the comparison data on the performance of the most vital types of farm products and foodstuffs in Russia and some countries of the world show that the increasing adjustments are required to be made to lots of indicators to successfully implement the policy of import substitution (with the share rated at about 1.3 trillion rubles to be achieved by 2020) and to ensure the national food security (Table 1).

It is worth pointing out that that despite the statement on accomplishment of the food sovereignty level in the Food Security Doctrine of the Russian Federation by such agricultural products as grain, potato, vegetable oil and sugar, many world countries show much higher performance in the industry with the farmland area much smaller as compared with those in Russia.

So, for example, the area of cultivated lands in such a small country as Belgium is 169.4 times less than in Russia, but the grain output per 1 person is 1.6 times higher. In terms of potato production, Denmark is 1.3 times ahead of Russia, despite the fact that the area of cultivated lands in this country is 84.7 times less. The similar results are reported in terms of production output for other types of agricultural products (Tables 1, 2).

Table 1. Production of most important types of farm products and foodstuffs in 2013 in Russia and in several world countries per capita, kg [11]

<table>
<thead>
<tr>
<th>Type of agricultural products</th>
<th>Russia</th>
<th>Australia</th>
<th>Austria</th>
<th>Belgium</th>
<th>Bulgaria</th>
<th>Hungary</th>
<th>Germany</th>
<th>Denmark</th>
<th>Italy</th>
<th>Canada</th>
<th>Netherlands</th>
<th>Poland</th>
<th>United Kingdom</th>
<th>USA</th>
<th>Finland</th>
<th>France</th>
<th>Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn**</td>
<td>721</td>
<td>1672</td>
<td>577</td>
<td>1150</td>
<td>1381</td>
<td>585</td>
<td>1628</td>
<td>272</td>
<td>2061</td>
<td>108</td>
<td>748</td>
<td>326</td>
<td>1388</td>
<td>757</td>
<td>1071</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Including wheat</td>
<td>409</td>
<td>998</td>
<td>188</td>
<td>700</td>
<td>515</td>
<td>305</td>
<td>738</td>
<td>121</td>
<td>1067</td>
<td>79</td>
<td>246</td>
<td>187</td>
<td>183</td>
<td>164</td>
<td>605</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Potato**</td>
<td>216</td>
<td>56</td>
<td>71</td>
<td>23</td>
<td>45</td>
<td>118</td>
<td>284</td>
<td>22</td>
<td>131</td>
<td>405</td>
<td>164</td>
<td>87</td>
<td>63</td>
<td>115</td>
<td>109</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Fruits*, berries*, citrus fruits and grapes*</td>
<td>24</td>
<td>156</td>
<td>113</td>
<td>76</td>
<td>130</td>
<td>29</td>
<td>12</td>
<td>276</td>
<td>23</td>
<td>42</td>
<td>109</td>
<td>6</td>
<td>94</td>
<td>4</td>
<td>129</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Vegetables* and melon and gourds</td>
<td>116</td>
<td>88</td>
<td>70</td>
<td>79</td>
<td>146</td>
<td>42</td>
<td>51</td>
<td>217</td>
<td>63</td>
<td>287</td>
<td>135</td>
<td>40</td>
<td>108</td>
<td>50</td>
<td>82</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>Salted cattle and poultry (carcass weight basis)*</td>
<td>62</td>
<td>196</td>
<td>106</td>
<td>29</td>
<td>82</td>
<td>99</td>
<td>337</td>
<td>67</td>
<td>123</td>
<td>159</td>
<td>99</td>
<td>57</td>
<td>134</td>
<td>72</td>
<td>87</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Milk*</td>
<td>211</td>
<td>416</td>
<td>403</td>
<td>179</td>
<td>178</td>
<td>380</td>
<td>910</td>
<td>183</td>
<td>239</td>
<td>74</td>
<td>330</td>
<td>218</td>
<td>289</td>
<td>430</td>
<td>385</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Eggs, pcs</td>
<td>287</td>
<td>175</td>
<td>200</td>
<td>165</td>
<td>253</td>
<td>167</td>
<td>250</td>
<td>229</td>
<td>225</td>
<td>637</td>
<td>260</td>
<td>39</td>
<td>301</td>
<td>203</td>
<td>246</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>Sugar (of domestic raw materials)**</td>
<td>31.5</td>
<td>149</td>
<td>59</td>
<td>0</td>
<td>12</td>
<td>54</td>
<td>77</td>
<td>6</td>
<td>3</td>
<td>60</td>
<td>50</td>
<td>21</td>
<td>23</td>
<td>16</td>
<td>69</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Pasta</td>
<td>6.8</td>
<td>...</td>
<td>...</td>
<td>2</td>
<td>8</td>
<td>3</td>
<td>0.4</td>
<td>...</td>
<td>...</td>
<td>5</td>
<td>...</td>
<td>3</td>
<td>...</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vegetable oils**</td>
<td>27.8</td>
<td>21.5</td>
<td>23</td>
<td>27</td>
<td>36</td>
<td>44</td>
<td>36</td>
<td>20</td>
<td>95</td>
<td>12</td>
<td>22</td>
<td>16</td>
<td>36</td>
<td>20</td>
<td>43</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Margarine products</td>
<td>3.5</td>
<td>...</td>
<td>...</td>
<td>1.3</td>
<td>...</td>
<td>4.8</td>
<td>11</td>
<td>...</td>
<td>...</td>
<td>15</td>
<td>6</td>
<td>3</td>
<td>...</td>
<td>3</td>
<td>...</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Cooking salt</td>
<td>3.4</td>
<td>477</td>
<td>...</td>
<td>...</td>
<td>232</td>
<td>...</td>
<td>48</td>
<td>311</td>
<td>389</td>
<td>110</td>
<td>96</td>
<td>128</td>
<td>...</td>
<td>96</td>
<td>...</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Animal oil</td>
<td>1.7</td>
<td>5.3</td>
<td>4.2</td>
<td>0.2</td>
<td>0.4</td>
<td>5.5</td>
<td>6.9</td>
<td>2</td>
<td>2.5</td>
<td>8</td>
<td>5</td>
<td>2</td>
<td>10</td>
<td>7</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes. **By 2020, the imported farm product supply is planned to be reduced as follow: meat of cattle and poultry - by 67.8%, milk - by 29.9%, vegetables - by 70.3%, fruit and berry products - by 20%, grapes - by 54.6%.

** With respect to grain, potatoes, vegetable oil and sugar, the desired level of food food sovereignty as specified by the Food Security Doctrine of the Russian Federation has been achieved.
Fig. 1. Share of the "Agriculture, hunting and forestry" in the structure of regional GRP of the Russian Federation entities for 2014 (compiled by the authors to: [10]).
The figures above indicate a variety of systemic issues, including the use of morally obsolete equipment and technologies in farm production, high physical depreciation of fixed assets (37% in 2014 as per Rosstat, Federal Service of State Statistics), immaturity of rural area infrastructure, low level of human capital asset development that impedes the industrial reequipment. Ultimately, the issues above serve as the reason for irrational use of cultivated lands and the extensive nature of the industrial progress.

The financial component is one of key factors of sustainable development in any sector of national economy. In this term, the agriculture is no exception. The financial status of farms remains unstable, as evidenced by parameters of a variety of financial ratios (Table 3). So, the value of working capital financed by equity to total assets ratio remains negative, despite the upward trends that means that entities do not have own resources available to finance their current activities (purchase of raw stock, materials, etc.), and, consequently, it indicates the demand in credit assets. Dependence on external sources of funding is also proved by the value of equity to total assets ratio (Table 3).

Yet, institutional bases are formed, the governmental share in the industrial development remains too low, in our opinion, and the applicable measures are often non-effective. The structure of investments in fixed assets allocated for agricultural sector development was analyzed to prove on inadequate involvement of government in this process (Table 4, Fig. 2). The major sources of financing are own and attracted assets of agricultural producers.

Amendments to the applicable legislation in terms of granting subsidies at the expense of the federal budget to reimburse expenses for the purchase of mineral fertilizers and chemical protection equipment, reimbursement of partial cost for insurance payments, as well as of part of the investment loan interest rate, stimulated attraction of credit resources by agricultural commodity producers. The share of borrowed funds in the investment structure in 2005–2008 increased, reaching its peak value, in 2007, that makes 61.6%. The scope of investments, on whole, showed upward trends, either. As for 1999 to 2015, three critical points may be highlighted where its decrease was required as follow: in 2004 – by 65.1%, in 2009 – by 16.4%, in 2015 – by 5.58%. However, if the negative trend of investments in 2014 to the agriculture development was due to the fall in grain prices and crop failure (production output decreased by more than 25% due to unfavorable agroclimatic conditions), in 2009 and 2015, the negative trend by this parameter related solely to the crisis processes in the economy and the decline in financial capacities of both economic entities and in the budget of the Russian budget system.

When it comes to the governmental involvement in the growth of industry on whole, then, despite the upward trend of budget allocations of the consolidated budget of the Russian Federation (Fig. 3), the share of investments in the capital stock at the expense of the federal budget, starting from 2005, did not exceed 5%, and in 2010–2013 it was a little bit greater than 2%. The involvement of RF entity budgets in the support to the industrial growth was even more inferior (Table 4).

Comparison of the volume of RF consolidated budget subsidies with the federal budget for 2006–2015 by the sub-section of the budget classification of expenditures "Agriculture and Fishery" that enables to report on the sensitivity of the federal budget to crisis processes in the economics. It was in 2009 and 2014, in the course of decline in demands and prices for hydrocarbon raw materials in foreign markets, where financing of the industry was abruptly reduced (Fig. 3–4).
Table 3. Some parameters characterizing the financial standing and financial performance of agricultural entities for 2013–2015 [12]

<table>
<thead>
<tr>
<th>Criteria</th>
<th>2013</th>
<th>2014</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current liquidity ratio*, %</td>
<td>155</td>
<td>160.9</td>
<td>181.7</td>
</tr>
<tr>
<td>Working capital financed by equity to total assets ratio**, %</td>
<td>-41.2</td>
<td>-38.1</td>
<td>-14.2</td>
</tr>
<tr>
<td>Equity to total assets ratio***, %</td>
<td>37.8</td>
<td>39.3</td>
<td>44.8</td>
</tr>
<tr>
<td>Number of profitable entities, thous.</td>
<td>4.3</td>
<td>4.1</td>
<td>3.7</td>
</tr>
<tr>
<td>Balanced financial result, bln rubles</td>
<td>60.9</td>
<td>181.1</td>
<td>280.1</td>
</tr>
</tbody>
</table>

Notes. *Current liquidity ratio – the recommended value is 200%; **Working capital financed by equity to total assets ratio – the recommended value is 10%; ***Equity to total assets ratio – 50 %.

Fig. 2. Graphical view of trends in volume and structure of investments in capital assets to be allotted to agricultural development by sources of funding for 1999–2015 (compiled by authors to: [13]).
Table 4. The structure of investments to the capital stock for agricultural development as per sources of funding for 1999 – 2015, % [13]

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</tr>
</thead>
<tbody>
<tr>
<td>Investments to fixed assets, total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<td>100</td>
<td>100</td>
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<tr>
<td>of them:</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>own funds</td>
<td>59.8</td>
<td>67.1</td>
<td>77.4</td>
<td>72.5</td>
<td>69.2</td>
<td>77.4</td>
<td>59.8</td>
<td>42.5</td>
<td>38.4</td>
<td>39.8</td>
<td>44.5</td>
<td>49.3</td>
<td>44.3</td>
<td>46.8</td>
<td>44.8</td>
<td>52.8</td>
<td>61.5</td>
</tr>
<tr>
<td>raised funds</td>
<td>40.2</td>
<td>32.9</td>
<td>22.6</td>
<td>27.5</td>
<td>30.8</td>
<td>22.6</td>
<td>40.2</td>
<td>57.5</td>
<td>61.6</td>
<td>60.2</td>
<td>55.5</td>
<td>50.7</td>
<td>55.7</td>
<td>53.2</td>
<td>55.2</td>
<td>47.2</td>
<td>38.5</td>
</tr>
<tr>
<td>of which: budgetary funds</td>
<td>6.6</td>
<td>8.5</td>
<td>5.6</td>
<td>5.0</td>
<td>4.1</td>
<td>5.6</td>
<td>4.3</td>
<td>3.1</td>
<td>2.7</td>
<td>3.5</td>
<td>3.6</td>
<td>2.3</td>
<td>2.4</td>
<td>2.0</td>
<td>2.3</td>
<td>3.3</td>
<td>…</td>
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<tr>
<td>including</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>the federal budget</td>
<td>3.0</td>
<td>3.9</td>
<td>2.0</td>
<td>2.1</td>
<td>1.7</td>
<td>2.0</td>
<td>0.7</td>
<td>0.5</td>
<td>0.6</td>
<td>0.9</td>
<td>1.2</td>
<td>0.7</td>
<td>1.0</td>
<td>0.7</td>
<td>1.1</td>
<td>1.9</td>
<td>…</td>
</tr>
<tr>
<td>budgets of RF subjects</td>
<td>3.2</td>
<td>4.3</td>
<td>3.4</td>
<td>2.8</td>
<td>2.3</td>
<td>3.4</td>
<td>3.3</td>
<td>2.5</td>
<td>1.9</td>
<td>2.4</td>
<td>2.3</td>
<td>1.4</td>
<td>1.3</td>
<td>1.2</td>
<td>1.0</td>
<td>1.3</td>
<td>…</td>
</tr>
<tr>
<td>local budgets</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>0.2</td>
<td>0.1</td>
<td>…</td>
<td>…</td>
</tr>
</tbody>
</table>

Fig. 3. Volume of the RF consolidated budget subsidies as per the item of budget classification of expenditures "Agriculture and Fishery" for 1999–2015, in bln rubles. compiled by authors to: [14]).

Fig. 4. Comparison of the RF consolidated budget subsidies with the federal budget for 2006–2015 in terms of the sub-section of the budget classification of expenditures "Agriculture and Fishery" in bln rubles (compiled by authors to: [15]).
Due to the growing global political and economic uncertainty and budgetary constraints, there is an urgent need to search for fundamentally new approaches to manage budget resources available at all levels of the RF budget system to ensure the governmental support to strategically important sectors (including agriculture), but also to raise the required sources of resource support (primarily financial) that will help to overcome the extensive development of the industry and ensure its functioning at a radically new level. Up-to-date treasury technologies offer chances to minimize budgetary risks when reducing budget revenues and are focused to address issues on the shortage of financial resources available by effective management of budget liquidity.

Treasury technologies for budget liquidity management and their role to achieve the budgetary risks reduction under global uncertainty

The financial and economic crisis of 2008–2009 of the subsequently chronic nature that lasts up to date, has boosted the likelihood of budget risks caused by high dependence of the Russian economy on the demand and prices for raw stock.

The budget risk is the potential failure to comply (in full or in part) with certain budget parameters, inefficient liquidity management of the budget account, as well as the inefficient use of budget funds. This is why the liquidity management was accentuated as one of the most urgent issues for discussion at the workshop "Treasury System Upgrading of the Asia-Pacific Economic Cooperation (APEC) Economies" held in March 2012 in Kazan.

The deviation from the cash budget is one of problems that arise when meeting budgets and that results in the liquidity shortage. Irregularity of cash payments that appear as "peak" payments at the end of each quarter and at the end of any financial year, generates risks of cash deficiency on unified budget accounts that synergize in a climate of global political and economic uncertainty.

A distinctive feature of distribution of public financial flows in the RF budget system is the significant concentration thereof in the federal budget. Thus, as per the reports on implementation of the consolidated budget of the Russian Federation and budgets of governmental extra-budgetary funds for 2015, the share of federal budget revenues in total revenue made 50.74%, budgets of governmental extra-budgetary funds – 34.33%, consolidated budgets of RF constituent entities – 34.57%, budgets of territorial state extra-budgetary funds – 5.9% [15]. Utilization of this model of distributive relations is one of reasons for budget imbalance of public and legal entities of sub-federal and municipal level that requires intergovernmental alignment through providing inter-budgetary transfers, attraction of budgetary credits to cover transient cash shortage that arise when executing budgets and utilizing state borrowings. Under the existing model of distributive relations, the fiscal capacity of regions and municipalities largely depends on the utilization of the federal budget capacity. This means that a decrease in its financial capacities involves destabilization in the development of regional and municipal social and economic systems and creates a threat of reducing the national competitiveness of Russia as a whole.

The consolidated balance of the RF subjects was analyzed to reveal that consolidated budgets of only 9 regions out of 85 subjects of the Russian Federation were in surplus in 2015. They include the Vladimir Region, Leningrad Region, Sakhalin Region, Tyumen Region, cities of federal significance recognized as RF subjects, namely Moscow, St. Petersburg, Sevastopol, as well as the Khanty-Mansi Autonomous Area and the Chukot Autonomous Area. It should be noted that consolidated budget surplus in Moscow for 2015 was 12.2 times higher than the surplus of the Tyumen Region, one of the most prosperous regional budget in terms of balance (+144,399.3 and +11,788.4 mln rubles, respectively). The remaining 76 consolidated budgets of the RF subjects were short in financial resources.

The highest deficit in the consolidated budget in 2015 was reported in the Krasnoyarsk Territory (-37,029.9 mln rubles), followed by Sverdlovsk Region (-17,545.3 mln rubles), Krasnodar Territory (-17,136.5 mln rubles.) [16]). The results of study of consolidated budget balance for the RF constituent entities for 2015 are shown in Fig. 5.

The consolidated budget of the Russian Federation is also in scarcity. As per the data of the budgetary reporting published on the official website of the Federal Treasury, the deficit of the consolidated budget of the Russian Federation as of 01.01.2016 amounted to – 2,819,493.3 mln rubles. [15].

It should be noted that today the world meets proactive institutions focused to ensure the governmental budget balance since the need to cover budget expenditures at the cost of revenue increasingly assumes not only the political and economic but also the social significance. Thus, the "Fiscal Compact" of the European Union adopted in 2011 specifies introduction of constitutional norms or framework laws known as "debt brakes" in the Eurozone states [17, cl.1]. The substance of these standards is the use of the "golden rule", namely, the requirements to ensure the budget balance. In March 2012, in Brussels, 25 of 27 states, as members to the Economic and Monetary Union (EMU), agreed to sign the Treaty on the Stability, Coordination, and Governance (TSCG). Initially, to ensure sustainability of public finance of the Eurozone states in 1997, the Stability and Growth Pact (SGP) was adopted.

2 The budget risk in relation to the federal budget is defined in the Order No. 383 of the Ministry of Finance of Russia dd. 10/19/2011 (as amended on January 20, 2014) "On the procedure for strategic monitoring of the quality financial management by the Ministry of Finance of the Russian Federation".

3 As per the Article 6 of the Budget Code of the Russian Federation No. 145-FZ dd. July 31, 1998 (as amended on November 30, 2013), the consolidated budget is the collection of budgets of the RF budgetary system in the relevant territory (excluding budgets of state non-budgetary funds) regardless of inter-budgetary transfers between these budgets.
Fig. 5. The results of study of consolidated budget balance of the RF constituent entities for 2015 in mln rubles: compiled by authors (to: [16]).

Deficiency (surplus) of the consolidated budget of the subject of the RF, mln rub.
Currently, the protocol annexed to the Treaty of the Functioning of the EU contains requirements to the limit size of the national deficit (not more than 3% GDP) and the upper limit of the government debt (not more than 60% GDP) (See TFEU art 126(2); Protocol No. 12, supra note 14, Art. 1) [18, cl. 2].

In the US, despite the statement by the Ministry of Finance on the need to increase the upper limit of the official debt, the Republican Party urged to make amendments to the constitution to ensure the budget balance whereunder the state budget expenditures should not exceed 18% of the national annual output [19, cl. 195].

In Russia, the requirements to balance budgets are regulated by the Section IV of the RF Budget Code4. It sets forth requirements to the volume of expenditures to serve the public debt of a constituent entity of the Russian Federation (municipal entity) that should not exceed 15% of the relevant budget expenditure volume.

The federal budget revenues significantly depend on oil and gas revenues, that, pursuant to provisions of the Article 96.6 of the RF Budget Code, include the federal budget return on tax payment for mineral production of hydrocarbon raw stock and export customs duties on crude oil, natural gas and petroleum products. The trend data for the share of oil and gas returns in the total volume of actual revenues of the federal budget is shown in Fig. 6. The lowest share of oil and gas return was reported in 2004 (30.19%), the peak value of this parameter was reported in 2014 when the share of oil and gas returns in the total revenue of the federal budget made 51.28%5.

The close correlation of the total volume of federal budget revenues with the volume of oil and gas return (Fig. 6) raises risks of failure to fulfill expenditure commitments funded with the federal budget against the unfavorable situation at the hydrocarbon market. While the federal budget, since 2014, is designed in view of program-based principles, the failure to fulfill the expenditure obligations primarily concerns governmental programs of the Russian Federation, including program costs associated with the support to agricultural producers. In this situation, destabilization risks arise of the industry potential growth as a whole.

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4 The requirements to the budget deficit limit are set forth for budgets only of the RF constituent entities and local budgets. As for the federal budget deficit, the standard specifying its upper limit is excluded from the Article 92 of the RF Budget Code. Pursuant to provisions of the Article 95 (as amended by the Federal law № 63-FZ dd. 26.04.2007), the federal budget deficit as approved by the Federal Law On the Federal Budget for the next fiscal year and the schedule date, may not be greater than the volume of non-oil and gas deficit of the federal budget.

The study of trends in the Urals crude oil prices offers to conclude that from January 2002 to July 2008 sustainable upward trends were reported for this figure to define parameters of the federal budget of those time. Having reached its peak in July 2008, namely, $129.45/barrel, crude oil prices declined for the next five months of 2008. In general, three critical points may be highlighted for the studied period where the crude oil prices were the lowest, that is, the Q1 2002 ($19.82/bbl), December 2008 ($38.50/barrel), January 2016 ($28.53/barrel) (Fig. 8) [21].

The years 2000–2008 should be considered favorable for the development of the Russian economics when the hydrocarbon prices showed steady upward trends, and the federal budget was adopted and implemented with the surplus (Fig. 9). At that particular time a range of measures were taken aimed to develop the human capital capacity, ensure the global competitiveness and financial stability in Russia. First of all, as initiated by the RF President, it refers to implementation of national projects of high priority since 2005, including the top national project “Development of Agrobusiness” to be subsequently transformed to the State Program for the Agriculture Development and Regulation of Agricultural, Raw Materials and Food Markets. During the sustained growth of economics, the Stabilization Fund was formed as part of the federal budget that was subsequently split for two funds – the Reserve Fund and the National Wealth Fund [22]. Pursuant to provisions of the Article 96.9 of the RF Budget Code, the major objective to form the Reserve Fund is to ensure the balance (deficiency payments) of the federal budget. The sources of the Reserve Fund (clause 3, Art. 96.9 of the RF Budget Code) include the extra oil and gas returns, provided that the accumulated assets of the Reserve Fund do not reach its rated volume (7% of GDP predicted) and revenues from the Reserve Fund management. However, due to abrupt decline of hydrocarbon prices, the effect of the cl. 3, Art. 96.9 of the RF Budget Code was suspended [23]. Until February 1, 2020, the returns on the Reserve Fund management are allotted to finance the federal budget expenditures.

![Fig. 8. Price dynamics for the Urals crude oil for 2002–2016, $/per barrel (compiled by authors to: [21]).](image)

![Fig. 9. The federal budget balance for 1999–2015, in mln rubles. (compiled by authors to: [24]).](image)
During the financial and economic crisis of 2009, the Reserve Fund assets were assigned to support the bank liquidity, to finance the federal budget deficit and to take anti-crisis measures in the territory of RF constituent entities. At that particular period, the volume of subsidies to support the regional budget balance increased by 4.2 times [20], since the revenue collection in the RF constituent entities (especially of raw stock) declined drastically (Fig. 10). For example, in January 2009, the regional budget of the Kemerovo Region had the shortfall of profit in the amount of 2 bln rubles. Facing the threat of cash deficiency on the unified account of the regional budget, the priority was given to the costs for remuneration, purchase of medicines, food, payment of utility fees, payment of scholarships, where the costs of construction, reconstruction, upgrading of facilities, including socially significant structures, were provisionally suspended.

By the late 2008, the balance of the Reserve Fund amounted to 9.8% GDP, and resulting from measures to ensure macroeconomic stability by spending about 3 trillion rubles, it made 4.7% GDP (by the late 2009). In late 2010, the Reserve Fund assets amounted to 1.7% GDP (Fig. 11). Nevertheless, against the price advance for hydrocarbon in 2010–2011 thanks to implementation of the policy on saving extra oil and gas returns by the Ministry of Finance, the scope of the Reserve Fund was increased to 3.2% GDP.

The experts of the Ministry of Finance of the Russian Federation hold a view that Russia will not be able to proceed to the Reserve Fund replenishment in view of predicted crude oil prices in the hydrocarbon market and the growth of the federal budget deficit up to 2020.

Fig. 10. The trend of the subsidy volume to align the fiscal capacity and to support measures to ensure budget balance for 2008–2015, in mln rubles (compiled by authors to: [20]).

Fig. 11. The trends of volume of the Reserve Fund assets in 2008–2016, in bln USD (compiled by authors to: [25]).
It is obvious that under the growing global uncertainty and budget constraints, the risks arise of cash deficiency and non-fulfillment of expenditure obligations of budgets that conditions the need to seek for brand-new approaches to manage the budget liquidity at all levels of the RF budget system.

One of the key principles of the budgetary system is the principle of cash unity and in compliance with provisions of Art. 38.2 of the RF Budget Code, it means the enrollment of all cash receipts and implementation of all cash payments from the single budget account. It was possible to implement this principle due to the technology of the unified budget account, that, as per the Art. 6 of the RF Budget Code, means an account (totality of accounts for the federal budget, budgets of state extra-budgetary funds of the Russian Federation) opened for purposes of the Federal Treasury with the Central Bank of Russia, separately for each budget of the budgetary system of the Russian Federation to register the budget assets and execute operations on cash receipts to the budget and cash payments from the budget.

The first step to address the issue of budget liquidity management was the Single Account Concept developed by the Ministry of Finance in conjunction with the Russian Treasury and approved by the Decree No.107-r of the Government of the Russian Federation dd. January 23, 2000.

Prior to implement provisions of the Concept, the federal budget assets were dispersed to income and expenditure accounts opened for the Federal Treasury Authorities (FTA) with the Bank of Russia (60% of accounts), in Shergbank facilities (38% of accounts) and in crediting institutions (2% of accounts).

In addition to the expenditure account of the federal budget, 4 accounts were used for revenue recognition and distribution only of the FTA to account returns on payment of:

1. taxes received from taxpayers and subject to distribution by the FTA in line with statutory regulations specified between budgets of different levels;
2. revenues of the federal budget;
3. revenues of the federal budget allotted to finance expenditures;
4. revenues of the federal budget transferred to the transit account to facilities of the Bank of Russia.

The Concept introduced the term - Single Treasury Account (STA) that is opened with any institution of the Bank of Russia and where assets are accumulated and transactions are registered carried out by federal government authorities to meet the federal budget.

One of fundamental features of STA technology was the account opening to distribute returns between budgets of the budgetary system of the Russian Federation managed by the Federal Treasury Departments (FTD) with institutions of the Bank of Russia that made it possible to combine functions of four profitable personal accounts previously opened with Federal Treasury Branches (FTB). Subsequently, when implementing provisions of the Art. 215.1 of the RF Budget Code that came into force in 2005, the unified budget accounts were opened for RF constituent entities and municipal entities.

In general, the application of STA technology allowed:

1. to ensure concentration of federal budget revenues and assets for STA 40105 "Federal Budget Assets";
2. to concentrate transactions for revenue recognition of different level budgets on the account 40101 "Revenue distributed by the FTA between the budgets of the budgetary system", opened at the level of the FTD and expense accounting of federal budget at the level of the FTD;
3. to ensure daily accounting of transactions on revenues and expenditures of the federal budget in the General Ledger of the Federal Treasury conducted at the level of the FTD.

The Federal Law No. 63-FZ dd. April 26, 2007 added an Art. 226.1 to the Budget Code of the Russian Federation on the Limited funding volume where the financial authority specifies the maximum amount of liability payment for the relevant period of the current fiscal year. In addition, the financial authority specifies events, approval and communication thereof to senior custodians, custodians and recipients. Limited funding volumes allow the liquidity management under conditions of strict budget constraints, especially in case of revenue shortfall to the unified budget account in view of crisis in economics and mitigation of the likelihood of cash deficiency on the unified budget account. The financial authority approves the limit for senior custodian by using the expert judgment and extrapolation methods, and the decisions may be informed on a quarterly basis with the detailed specification by months within each quarter, in addition. In other words, acceptance of budget commitment by spending unit through conclusion of contracts or agreements with legal entities and individuals takes place within the limits of levels proved, and the assets are granted as part of funding of the budget level proved that may be paid in parts until the limit amount is reached.

Limited funding volume is paid to recipients of budget funds of the RF constituent entities and local budgets, and to the recipients of federal budget funds [26, 27].

The possibility to allocate the federal funds to deposits and their transfer to trust management (Art. 256 of the RF Budget Code) allowed initiation of the budget liquidity management system in RF in 2008 of the Single Treasury Account. However, the system of restrictions under provisions of the article above does not allow the placement of free cash assets of RF subjects with the estimated share of inter-budget transfers from the federal budget (excluding subventions and subsidies from the RF Investment

6 At the level of FTD, accounts were opened in each RF constituent entity with the Bank of Russia facilities flagged 40101 to distribute revenues received between budgets of the budgetary system of the Russian Federation, as well as accounts flagged 40105 used to account expenditures of territorial executive bodies that were recipients of federal assets.

7 The limit funding cannot exceed the amount of the limits of budget obligations proved for the spending unit (note by O.V.).
Fund) within two of the last three fiscal years did not exceed 20 percent of the consolidated budget own revenues.

The innovative approach to budget liquidity management by the FTA includes the provision, since 2013, of subventions, inter-budget subsidies and other inter-budget transfers for special purpose under the actual need. The implementation of this procedure is set forth in cl. 7 of the Decree No. 1272 of the RF Government dd. December 10, 2012 (as amended on 04.09.2013) on measures to implement the Federal Law On Federal Budget for 2013 and Scheduled Period 2014-2015 and allows to exclude unused balance of inter-budget transfers at the end of any fiscal year on unified accounts 40201 "RF Subject Budget Funds". At the same time, expenditures of budget fund recipients for actual needs does not commit to prolong the execution time of payment document and shortens the period of target fund receipt to the regional budget income.

This mechanism is focused on execution of powers of senior custodians of federal budget funds by the territorial bodies of the Federal Treasury and wit this purpose, a personal account flagged 14 is opened to pay liabilities for expenditures of recipients of the RF subject budget sourced by inter-budget transfers from the federal budget to ensure financial security. At the same time, each subsidy, subvention, each other inter-budget transfer of target purpose is assigned with the appropriate target codes which are at all times specified in the expenditure schedule, based on which the personal account flagged 14 accounts for budgetary data (budget allocations, limits of budget obligations and the limit budget level) and in the application for cash expenditures to ensure the adequate accounting for transactions on the personal account and the unified budget account and to form the budgetary reporting on transferred and used inter-budget transfers for targeted purpose.

In 2014, the procedure of transfer provision under the actual need was implemented at the municipal level with the institutional basis as the Order No. 5n of the Treasury of Russia dd. March 26, 2014. Similar orders of the Treasury of Russia were adopted in 2015 and 2016 [28].

However, despite the implementation of this mechanism, on unified accounts flagged 40201 "Funds of the RF Subject Budgets" totaling 85 currently opened with the Bank of Russia, and unified accounts flagged 40204 "Local budget Assets" amounting to over 22000, significant balances of inter-budget transfers accumulate at the beginning and the end of any fiscal year.

It should be noted that the balance of inter-budget transfers is formed due to subsidies, either, to agricultural producers from the federal budget. The information on the movement of inter-budget transfers funded by the federal budget in 2015 is shown in Table 5 [15].

Table 5. Provision of inter-budget transfers to budgets of RF subjects in 2015 by the federal budget, in mln rubles

<table>
<thead>
<tr>
<th>Balance as of 01.01.2015</th>
<th>Total</th>
<th>Including those the need for which is proved</th>
<th>Received from FB</th>
<th>Cash flow</th>
<th>Inter-budget transfers for past years restored</th>
<th>Unused balances for past years is returned to FB</th>
<th>Returned to FB within the volume of needs in consumption</th>
<th>Balance as of 01.01.2016</th>
</tr>
</thead>
<tbody>
<tr>
<td>125 980, 13</td>
<td>109 343, 39</td>
<td>952 738, 35</td>
<td>988 424, 21</td>
<td>3 657, 85</td>
<td>132 953, 60</td>
<td>111 278, 22</td>
<td>72 276, 73</td>
<td></td>
</tr>
</tbody>
</table>

This means that methods to assess the need in inter-budget transfers require to be adjusted, on the one hand, and on the other hand, the concentration of resources above on the same account would allow their placement to financial instruments and, thereby, receipt of additional return on free cash management. In our opinion, the use of this methodology, namely, payment of the limit budget to recipients for purposes of expenditure would be rational not only as part of the regulation of the fund transfer from one level of budgetary system to another, but also in terms of the specific budget, since, as proved by more than a decade of practice of one of this article authors in the system of the Federal Treasury, budget data, including limit budget amounts paid to recipients are often of demand in full. Definitely, provisions of Art. 242 of the RF Budget Code do not oblige recipients of budget funds to “zero” accounts thereof based on which the budget subsidies, budget obligation limits and funding limits for the current fiscal year cease to be effective on December 31. Hereat, when forming the consolidated quarterly budget breakdown 8, the budget data are distributed by the financial authority between the senior custodian of budget funds, resulting in “pulling” portions of the budget data by the particular senior custodian (and further by its accountable institutions) which may stay non-demanded in future. Thus, unsatisfactory quality of financial management by budget fund custodians generates, among the others, the problem of ineffective management of budget liquidity on unified budget accounts.

8 The consolidated quarterly profile is the document compiled and maintained by the financial authority (management authority for the state extra-budgetary fund) to arrange the budget execution by budget expenditures and sources of financing of budget deficit (Art. 6 of the RF Budget Code No. 145-FZ dd. July 31, 1998 (revised on 11/30/2016).
The analysis of the budgetary reporting on the federal budget implementation by expenditures indicates that when clarifying the consolidated quarterly profile and allocating extra budgetary assets to federal budget custodians, they are often used in part. There may be several reasons for this. One of them, already mentioned above, is the low quality of financial management. So, as per the results of monitoring the quality of financial management by the federal budget custodians as of July 1, 2016, the Ministry of Agriculture of the Russian Federation ranked 88th in the rating of 102 liable [29]. The assessment of financial management quality as per the method by the Ministry of Finance of the Russian Federation is conducted in several orientations as part of the approved system of parameters for each of them. So, the budget execution in terms of expenditure is assessed by such indicators as completeness, timeliness of acceptance and execution of budgetary obligations, deviation from the cash budget for federal budget expenditures, quality of management of federal budget funds in terms of inter-budget subsidies and subventions, subsidies and investments to legal entities and other.

Another reason is the time scarcity to hold competitive procedures and conclude government contracts in line with Federal Law 44-FZ [30], since budget recipients are often informed on the budget data by the financial authority at the very end of the fiscal year where there is short of time to execute competitive procedures.

The compliance with the cash budget is impeded by the delay in execution terms by contractors for concluded state (municipal) contracts that negatively affects the uniformity of cash payments from the unified budget account, and, therefore, forms the liquidity deficit.

Irregularity of cash payments from the unified treasury account is one of the urgent challenges announced in budget statements by the President of the Russian Federation in early 2000s, and, despite the improvement of treasury technologies, it remains urgent.

However, for the sake of justice, it should be noted that the irregular budget execution is specific not only for Russia but for other states either since, at the end of the fiscal year, most liabilities are fulfilled under most contracts. Therefore, for example, in Denmark and the Netherlands, it is allowed to transfer the portion of unused budget subsidies for the next year. In France and Sweden, the transfer limit for the next financial year is specified but not more than 3% of the total amount of subsidies allotted [31, p. 49].

In Hungary, to ensure the uniformity of budgetary expenditures, no more than 1/12 of fund allocation as provided for in the budget law is allowed per month, and the need to exceed the amount fixed is approved by the government [32].

In 2015, the document was adopted that, in our view, is of high significance to improve the efficiency of budget liquidity management under conditions of global uncertainty. It is referred to the Concept of budget payment system reforming [33]. The need in development and adoption of this Concept are largely due to a range of problems related to budget liquidity management, including:

- dispersal of budgetary funds to numerous accounts totaling over 50 000 in number;
- concurrent duplication of operations on income distribution between budgets of the RF budget system on accounts opened for the Federal Treasury with the Bank of Russia and personal accounts opened with territorial FTAs;
- the limited list of instruments to allocate the free budget liquidity on unified accounts of budgets of the budget system to financial instruments;
- inadequate level of income distribution efficiency from the account flagged 40101 "Incomes distributed among budgets of RF budget system" (more than three days in some cases)\(^9\);
- lack of budgets with revenue administrators, as well as with entities that deliver governmental and municipal services, urgent information on the arrival of funds to accounts, including the information on personal accounts opened with financial institutions;
- significant volume of transactions with cash assets resulting in difficulty to monitor the proper use of budget liquidity.

The main objective of the Concept is to improve the management efficiency of free cash balances of budgets.

As part of the Concept implementation, accounts are planned to close stage by stage that are previously opened by territorial FTAs with territorial offices of the Bank of Russia with subsequent opening thereof with the Bank of Russia to ensure accumulation of budget liquidity on the Unified Bank Account of the Treasury of Russia.

Pursuant to provisions of the Concept of the Budget Payment System Reforming, the transition to the Unified Bank Account of the Treasury of Russia will ensure the possibility to target cash balances\(^11\) and will

\(^9\) The status of the current system of budget payments is described by multiple accounts opened with territorial offices of the Bank of Russia by the territorial FTA, namely, accounts to account assets arriving for transient disposal of federal state and budgetary institutions; funds of budgetary, autonomous and other organizations owned by the government; budget funds of RF subjects; funds arriving for transient disposal of state and budgetary institutions of the RF subjects; local budget funds, etc., which finally result in dispersion of the budget liquidity.

\(^10\) It should be noted that, in line with provisions of the Art. 40 of the RF Budget Code, cash assets are deemed to arrive to income of the relevant budget since the date of asset crediting to the single account of this budget. Thus, the delay in schedule to distribute return that arrive to the account 40101, or the delay in asset arrival clarification where, for example, the income code, name of the budget revenue administrator, etc. is wrongly specified, it contributes to the growth of budget liquidity deficit on the unified accounts of budgets, and, consequently, it forms risks of non-fulfillment of budgetary obligations.

\(^11\) The targeting of cash balances on the Unified bank account of the Treasury of Russia as per the Concept is the management of the daily balance amount on the unified bank account by monitoring monetary liabilities of an entity whose personal accounts are opened with territorial FTAs and liquidity provision. The calculation of daily balance and prediction of cash balances on the unified bank account of the Treasury of Russia will be carried out by execution of payment schedule. The data for payment schedule will be contained in cash budgets to meet budgets of the budgeting system of the Russian Federation sent to the Treasury of Russia.
also enable usage of excess liquidity to generate additional return on operations to place free cash in financial instruments.

It is obvious that targeting of cash balances on the Unified Bank Account of the Treasury of Russia predetermines the need to forecast the demand for such funds not only in relation to the unified federal budget account, but also at the level of unified accounts of the budgets of RF subjects and municipalities. Financial authorities, chief administrators (administrators) of budgetary funds of sub-federal and municipal levels and recipients should be involved in this process.

For purposes to target the liquidity on the Unified Bank Account of the Treasury of Russia, the concept and the prototype of the "Cash Management" subsystem are planned to develop along with main functional requirements to the "Cash Planning" module of the prototype of "Cash Management" subsystem under the state integrated information system "Electronic Budget".

CONCLUSIONS

In general, the use of treasury technologies studied above is focused to address issues related to budget constraints and liquidity deficit under conditions of growing global political and economic uncertainty. Moreover, the transition to the new technology of the Unified Bank Account of the Treasury of Russia will allow to target cash balances and use the excessive budget liquidity to obtain additional budget revenues through placement thereof to financial instruments. In this situation, it is possible to transit to the policy of creating an innovation and investment-oriented budget deficit by channeling budgetary allocations for re-industrialization of strategically important industries, including agriculture, to ensure their compliance with the best industrial practices of the world's leading countries. The similar approach was proposed by Keynes in his work The General Theory of Employment, Interest and Money [34], that proved that active governmental participation in the development of economics, especially under the crisis, based on creation of the investment-oriented budget deficit and direct public investments in the economics (in our case, in agriculture), will not only increase the confidence of private investors to governmental authority performance, but will finally ensure the formation of multiplicative economic and social effects.

Ultimately, the development of tools to manage budget liquidity and, thereby, the reduction of budgetary risks (primarily, the risks of non-fulfillment of expenditure obligations of budgets of the RF budgetary system due to the decline in revenue receipts) will contribute not only to its retention but also to an increase in the share of governmental participation in the development of strategically important sectors, including agriculture, under conditions of global political and economic uncertainty, and the growth of Russia's national competitiveness as a whole.

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FORMATION OF AGRO-INDUSTRIAL CLUSTER ON THE PRIORITY SOCIAL AND ECONOMIC DEVELOPMENT AREA OF THE MONO-INDUSTRY TOWN


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Abstract: Issues on the development of mono-industry towns in Russia through diversification of economics thereof may be addressed by formation of the priority social and economic development area (PSEDA). By the results of analysis of conditions to create intraregional (municipal) industrial clusters within the PSEDA mono-industry towns, the feasibility of such clusters is justified to turn into the priority residents of PSEDA, but also to obtain the synergistic effect of taking PSEDA advantages and the cluster approach in diversifying the economies of mono-industry towns. In contrast to previous definitions, the authors consider the intraregional (municipal) industrial cluster as the concept created with favorable involvement of regional and municipal authorities to develop the cluster strategy and use favorable conditions to expand private enterprises, association of entities to implement projects on diversification of mono-industry town economies and investment projects that meet the PSEDA requirements. The principles of PSEDA-based cluster formation in mono-industry towns are formulated. The most significant factors of sustainable development of clusters are highlighted to address mono-town problems. The stage-by-stage creation of municipal clusters proposed by authors is based on their ability to emerge during the extensive market mechanism performance and includes stages to assess the potential to form and develop cluster formations, but also the stages to identify the needs of participating entities in the course of particular interaction, creation and development of entity networks. The analysis of existing agglomerations, systematization of SWOT analysis findings, assessment of factors contributing to cluster formation offered the chance to determine the perspective for the agro-industrial cluster development in Yurga in the Kemerovo Region. The study results represent the particular contribution to the cluster theory, regional economy in terms of development of tools to form municipal industrial clusters within the PSEDA for the purpose to diversify economies of mono-industry towns. The practical significance of the research is the possibility to apply the study results in the activity of regional and municipal authorities when identifying intraregional agglomerations, creating cluster formations as PSEDA mono-town residents.

Keywords: Mono-town, cluster, development, the priority social and economic development area, diversification

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INTRODUCTION

The socio-economic development of mono-industry towns directly depends on functioning of the city-forming enterprise (or a group of related enterprises). For the period from 2008 to 2015, as per various estimates, 200 to 500 settlements belong to RF mono-towns. With the reduction of mono-industry towns of the list approved by the government, the actual number of mono-industry towns and, in particular, the problems they accumulate, is not reduced from 335 in 2009 to 319 in 2015. Options for mono-industry town development: inertial development causing the liquidation of the city-forming entity and population resettlement, upgrading of the city-forming entity with retention of its city-forming purpose, diversification of the mono-industry town economy. Pursuant to the Federal Law No. 473-FZ dd. March 30, 2014 On Priority Social and Economic Development Area in the Russian Federation” [1] and THE Government Decree No. 614 dd. June 22, 2015 On peculiarities to create priority social and economic development areas in the territories of mono-profile municipal entities of the Russian Federation (mono-industry towns)” [2] the tool to address social and economic problems of mono-industry towns is the creation of priority social and economic development areas (PSEDA) based in mono-
towns with the most tough social and economic situation. Despite the PSEDA, along with clusters and special economic zones, are considered as mechanisms to stimulate industrial and innovative development, the authors assume that creation of intraregional (municipal) industrial clusters in the territory of monotowns as priority ("anchor") residents can afford the synergistic effect by benefiting from PSEDA and cluster approach. The economic meaning of clustering is to take advantage of the synergy that arise during interacting between related industry entities concentrated in one territory, and public and private sector organizations. The constructive partnership of all stakeholders in the development of local economy is the defining feature of the cluster. The clusters formation, even during the crisis, boosts the economic growth in territories, contributes to overcome technological backwardness. There is an opinion that cluster formation, involving entities from more than one municipal formation, can strengthen the mono-profile of towns [3]. However, there are examples of effective practice of forming intra-regional clusters. For example, the auto-industry cluster in the Kaluga region (developing based on the governmental support, in particular, tax incentives, access to infrastructure, investor support by administration), "Integrated development of the Lower Angara region" cluster (financed from the federal and regional budgets, banks and enterprises). In this regard, it seems that it makes sense to identify and develop associations of enterprises with the potential to transform into intra-regional clusters as part of PSEDA.

Despite the experience of cluster creation in the Russian Federation, there is a lack in practical formation as part of programs to create PSEDA in mono-industry towns. In addition, the term of cluster is not defined when applied to forms of organization for the purpose of PSEDA creation and development. The practice of cluster formation was reviewed to evidence that they may be formed, firstly, by natural means, as a consequence of gradual development of the certain area of concentration based in the specific territory, and secondly, as a result of purposeful implementation of cluster-forming events. Dirigiste and liberal models of clusters are specified as per these criteria: The dirigiste model is known to assume cluster formation through governmental support. Within the liberal model, the cluster emerges as a result of market rules, and the function of federal authorities is reduced to limiting barriers to its natural development [4]. Both models do not associate the cluster with special economic zones. However, it should be assumed that creation of special conditions favorable for the business development aimed, in particular, to addressing social and economic issues of mono-industry towns, for example, priority social and economic development areas, is the factor initiating the successful emergence and further development of clusters as elements (residents) of such territories. This is how the relevance and practical significance of this study is specified.

OBJECTS AND METHODS OF STUDY

The research object is cluster projects, economic relations of agrobusiness entities of of the mono-town, experience of cluster formation in industry.

Studies of national and foreign scientists primarily focus on the rationale to identify cluster groups, however, the potential of entities, in particular mono-towns, to become the cluster member is not studied, the methods of cluster formation are associated with methods of their identification only [5, 6].

Theoretical and methodological provisions of the cluster theory, official statistic publications, expert opinions form the information base of the research. The calculation-analytical method, system analysis, and method of expert appraisal are used.

When developing the principles of methodological approach to PSEDA-based cluster formation in mono-industry towns, the following provisions of theoretical concepts and studies were taken into account: the opportunity of more effective internal control based on internal information, regulation and coordination of business activities of merging enterprises as a result of intracorporate financial market formation (concept based on the intra-company capital market); efficient creation of networks of suppliers, producers, consumer networks and networks of technological cooperation (D. Ernst); advantages to form industrial chains, commodity chain, supply chains and the creation of value chains (E. Yordon, M. Christopher, T.J. Gallin and M. Hordon, M. Garrett and P. Ducege).

In the methodology for cluster formation analysis, methods for their detection and identification, methods for evaluation thereof and methodological approaches to assess their effectiveness are distinguished. The totality of methods to detect and identify cluster formations in the territory includes the expert assessments, calculation of localization coefficients, factor analysis, statistical cluster and discriminant analysis, use of production inter-branch balances, etc. To determine economic agglomerations capable of cluster forming, tradable or export-oriented industries are determined [7], the coefficient of sectoral employment localization is calculated as the ratio of share of this industry in production structure to the specific share of the same in the country. Similarly, the production localization factor, ratio of sectoral localization by labor productivity, investment and other indicators can be determined [8]. The clusters may be assessed based on SWOT analysis, analysis of industrial potential, methods to evaluate the effectiveness of investment projects, and others. As part of this study, expert assessments, SWOT analysis, assessment of potential of mono-industry sectors, and evaluation of investment project effectiveness were used to locate and identify, as well as to assess cluster structures.

RESULTS AND DISCUSSION

As the economic term, the cluster is a totality of enterprises concentrated on the specific territory, interrelated, but performing in different sectors. And the core of cluster is that its members complement each
other and strengthen their competitive advantages and those of cluster as a whole.

In the concept of M. Porter [9] the interaction between cluster members is distinguished (main manufacturing companies, auxiliary (associated) industries, universities, research organizations and government agencies). The cluster is a more complex formation as compared to a simple association of entities for joint activities, since it involves cooperation through participation in value creation systems, as well as competition.

R. Bro defines the cluster as “the intersectoral concentration of entities that create jobs, export goods and services, have common basic economic needs and unite the public sector of economic development, legislature of different levels, universities, colleges, educational community, funds and all other stakeholders” [10].

The cluster is the form of network intercompany interaction, and unlike entrepreneurial networks, it unites a wider range of embers, including support institutions, production and commercial structures (among them manufacturers, suppliers, as well as higher education institutions and scientific organizations). Within the cluster, members may be associated both by sectors and regions (interindustry).

The cluster member may be a focal enterprise (the core firm), key players, small and medium-sized businesses, supplier agencies, sales intermediaries, trading companies, representatives of workers (trade unions), investment companies, investors, capital investors, financial institutions, local administrations, supporting enterprises, universities, research organizations and think tanks being the part of the cluster companies. It should be noted that the ideas on focal networks with the involvement of a key player are well understood in Russia, but the capacity of small and medium-sized business is underestimated.

The intraregional (municipal) industrial cluster created based on PSEDA mono-town is proposed to be considered as: tool to structure the industry and its network organization; association of organizations, formed to implement projects to diversify the mono-town economy and investment projects meeting PSEDA requirements; network association of industry-related enterprises and organizations in the territory of a mono-industry town; a type of territorial cluster, regional industrial cluster, industrial district.

Its features are as follow:
– combination of competition and cooperation, market and organization;
– extensional and local economic structure, where socio-cultural and production and engineering factors interrelate to ensure competitiveness and activity;
– the focus of industrial entity is characterized by the focus of economic and entrepreneurial activity and limited by geography (municipal district, urban district);
– participants are the mono-industry town enterprises with the area of concentration in production of competitive products, suppliers of raw materials, services, cluster infrastructure creating in aggregate the final product and added value;
– availability of internal competition, that distinguishes the cluster against integrated entities.

The most successful and dynamically developing clusters formed based on special economic zones, technology parks and business incubators include clusters in mono-industry towns: cluster of automotive industry - Tolyatti and Naberezhnye Chelny, creation of “titanium valley” in the Upper Ufaley in the Sverdlovsk region, a chemical cluster in Nizhny Tagil, a wood processing cluster using the latest technologies in the city of Sokol, Vologda region and others.

Having analyzed the structure of clusters of mono-profile towns in the Sverdlovsk region, the specialists of the Ural State University compiled a list of most promising new industries for each single-industry town. So, the following industries were named for Nizhny Tagil: manufacture of electrical appliances, pharmaceutical industry, business services, jewelry industry.

The most significant factors for the successful development of clusters are: quality management [11]; mechanisms and organizational forms for knowledge accumulation and dissemination and social capital accumulation [12]; presence of at least 30–50 profile companies in the cluster to realize the potential of innovation diffusion [13].

To describe the communities of technologically related sectors in France, the term “dies” was widely used [14] as the form of interaction of of innovative cluster features. The term “clusters of innovation” has gained a wide popularity among public and private sector leaders after formation of the US cluster named “Clusters of Innovation” [15]. It well reflects the fact that all the world companies have to compete not only in and not so much in terms of productivity as in terms of the ability to innovate.

The methodology and implementation of cluster policy in Russia correspond to conceptual basis of similar European programs on whole, especially of French and German origin [13]. Since 2012, the Ministry of Economic Development of the Russian Federation has competitively selected projects for cluster development in the Russian regions. Around 100 cluster initiatives took part in the competition, 25 of them were selected for pilot support. In 2013–2014, the amount of 3.8 billion rubles was allocated from the federal budget for cluster development on co-financing terms from regional budgets. So, the innovative territorial cluster in the sphere of information and telecommunication technologies of the Novosibirsk region received 269 million rubles, and the information technology cluster in St. Petersburg – 1.3 million rubles. The average size of subsidy for clusters was about 100 million rubles [16].

An analysis of study results of Russian pilot innovation clusters [17] held in 2015 using the European Cluster Improvement Initiative showed the following:
– clusters are mainly located in Russian regions with a high level of innovative development (out of 21 test
clusters, 13 (62%) are based in "strong innovator" regions, 5 (24%) – in "medium-strong innovator" regions, 1 cluster is in the region of "medium innovator" and 2 (9.5%) – in "medium-scale innovator" regions) [18];
– in 13 clusters out of 21 the number of participants was less than 50, and less than 30 in 6 clusters;
– 11 new clusters are specialized in new industries (information technologies, bio-pharmaceuticals and new technologies), while 12 clusters can be referred to traditional high-tech industries founded in the Soviet time (production of aircraft and space vehicles, shipbuilding, nuclear and radiation technology, chemistry and petrochemistry).

Since a large share of Russian clusters is created based on former Soviet enterprises in conventional high-tech industries (aerospace complex, nuclear technologies, etc.), one of their features is a small number of small and medium-sized businesses that act as an active part of foreign clusters created. However, there is diversity among a small number of innovative clusters selected by the Ministry of Economic Development of Russia for subsidization as follow:
– clusters formed of members around large companies (aerospace cluster in Samara);
– networks joining small and medium-sized enterprises (information and pharmaceutical clusters in St. Petersburg and Novosibirsk);
– association of enterprises around the research institute ("Biotechnological Innovative Territorial Cluster "Pushchino") or leading universities (Cluster "Fiztekh XXI" in Dolgoprudny);
– formed in Closed Administrative Territorial Units (Sarov, Zheleznogorsk);
– created based on large agglomerations.

By the extent of impact on the regional and national economics, on whole, the multi-profile Kamsky Innovative Cluster in Tatarstan, clusters of information and communication technologies in St. Petersburg and Novosibirsk, regions, as well as the Samara aerospace and Bashkir petrochemical innovation territorial cluster (ITC) are ranked first as per the study results. The nuclear-innovative cluster in Dimitrovgrad in the Ulyanovsk region, the multiprofile cluster of the Tomsk region, the Zelenograd cluster of microelectronics (Moscow) and the engineering lighting cluster in Mordovia are distinguished by the interaction intensity within the cluster, namely, as per the share of participants in joint projects, number of joint innovation projects and business projects. By the professionalism criteria of the managing company, the multisectoral cluster in Tomsk, the cluster of pharmaceuticals, biotechnology and biomedicine in Kaluga, the nuclear-innovation cluster in Dimitrovgrad, ICT cluster in Novosibirsk and cluster of rocket engine building in Perm are ranked first.

The following dependencies are revealed: there is a correlation between the volume of cluster financing through the Ministry of Economic Development of Russia with the level of integration of its participants and the extent of cluster impact on regional development; there is no significant correlation between the support volume and the quality of cluster management [17].

Apart from cluster success, it is necessary to highlight the problems of their development in Russia. So, the cluster development is limited with the lack of knowledge and inability to apply best world practices locally, rapid result orientation, difficulties with investment raising, obsolete and worn-out fixed assets, human resource problems, and poor work-out of the strategy in terms of development priorities choice. Almost all sectors running in the territory are chosen as key areas of growth to result in dispersion of forces, lack of resources to implement all projects.

A particularly significant problem is the weak innovativeness of formed clusters, since the national economy remains weak-responsive to innovations. Among the important reasons the quality of the institutional environment and the specifics of internal industry markets should be accentuated. As a rule, companies are willing to invest in innovations only if the term for innovation and new product marketing is feasible within a year. This is not enough for breakthrough innovations. Even innovative entities are poorly cooperated in terms of creation of new knowledge, technology transfer and interaction with scientific organizations. In addition, the importance of existing barriers between the science, innovation, education and real economic sector should not be excluded, the growing differentiation between sectors in terms of their technological development, regional polarization by innovative performance.

In addition to problems and limitations in cluster development in the Russian Federation, the risks existing in the sphere of cluster formation and cluster policy should be systematized. For example, the global experience shows that when the cluster formation initiated exclusively by the government faces one of major risks, that is the failure to consider business development trends, as well as its economic interests. The "large-scale construction in the open field occurs initiated by officials oriented toward trendy issues" [19]. This results in the artificially created cluster that exists until the state support is granted. Due to certain artificially created cluster initiatives considered by regional authorities as a tool to ensure state support, horizontal links are poorly formed in Russian clusters, the member cooperation is not developed.

The Russian risks of cluster approach execution match those risks highlighted by foreign experts. In particular, Man-Wen T. and Vojer R. [20] focus on the most significant risks faced by foreign governments when forming and promoting cluster development: change of macroeconomic conditions, weak cluster innovation due to the lack of production mechanisms and adaptation of new knowledge, insufficient development of external and internal scientific and technological links that weakens the synergistic effect of clustering and use of inefficient management techniques.

In addition, risks of opportunistic behavior of cluster members, personnel risks (shortage of specialists of the required qualifications to support the cluster entity activities), logistical and marketing risks
should be highlighted. There are also risk groups produced by governmental authorities. For example, infrastructure risks manifested in case of insufficient provision of cluster members with transport, energy, communal and other infrastructure for cluster members, institutional risks that are due to inconsistency of measures of scientific and technical, industrial, regional, socio-demographic, educational policies, resource risks associated with inadequate or inefficient use of budgetary funds.

PSEDA creation in mono-towns is aimed at creating conditions to attract investments avoiding mono-dependence. By implementing projects with multiplier effect, it will be possible to improve the life quality of population by creating the new social infrastructure, work places and by increasing the tax base. The creation of the sustainable system of investment attraction and investment projects implementation will ensure solution of tasks of sustainable social and economic development for the long term. In addition, the PSEDA creation allows solving problems as follow: attracting high-tech enterprises of processing industries with high added value, the growth of competitiveness of the territory by creating conditions to attract investors to the region, including foreign ones and creation of new, up-to-date, export-oriented production, reduction of unemployment through redistribution of labor resources available, growth of tax and non-tax revenues (for example, return of old and emergence of new taxpayers).

PSEDA are created in mono-industry town territory with the most difficult social and economic situation. So, for example, the Yurga municipal district of the Kemerovo region (hereinafter referred to as the “mono-town Yurga”) is listed among single-profile municipal entities of the Russian Federation (mono-industry towns) and depending on the risk of their socio-economic deterioration, refers to Category 1 - mono-profile municipal formations of the Russian Federation (mono-industry towns) with the most difficult social and economic situation (including in interrelation with problems of the city-forming entity functioning). The unemployment rate increased from 1.6% to 2.1% between 2000 and 2008 in the mono-town Yurga in the Kemerovo region. By 2009, the level was 3.6%, and by 2016, the figure almost doubled and amounted to 6.4%. In 2016, the staff double reduction is planned and dismissal of more than 1750 peoples at the town-forming entity, that is, the Yurginsky machine-building plant. The Yurginsky Machine-Building Plant LLC faces significant difficulties to obtain orders and, as a result, production volumes have significantly decreased. The city does not dispose of sufficient internal sources for budgeting. In April 2015, the Agreement was signed between the Mono-Town Development Fund and Administration of the Kemerovo Region. To annul infrastructure constraints and develop investment projects, Yurga was allocated assets in the amount of 373.5 mln rubles, and 139.5 million rubles for the construction of a sewage collector.

Formation of the program for PSEDA creation and development in the mono-town requires justification of the list of economic activities that may be internal triggering points. The cluster approach may be used for justification. The cluster approach is one of ways to increase the competitiveness and economic development of territories. In addition, in the paradigm of cluster ideology, the priority today is given to restructuring of the area economy, in particular, to supporting diversification.

It is obvious that single-industry clusters around one or a group of entities may be formed in single-industry towns. Moreover, due to internal structuring, they may be more resistant to the impact of risks associated with external environment of cluster performance. However, failures in cluster functioning may result in the destruction due to weak diversification of the economy of the territory.

When using the cluster approach to form the PSEDA-based mono-town program, one should consider the foreign practice of cluster management of the European Cluster Excellence Initiative [21], the research results of industrial cluster state management, formation of business clusters and high-tech clusters [22, 23, 24, 25, 26, 27], and factors of their sustainable development revealed during the study of national practice of clusters functioning [17].

Prerequisites to create intraregional (municipal) industrial clusters within the PSEDA mono-towns: lack of own opportunities with entities to arrange the effective production activities based on introduction of innovations; the need for economic diversification; the demand for production upgrading; import substitution and the possibility to use favorable conditions for the private entrepreneurship development.

The scenario approach to create municipal clusters based on PSEDA assumes the priority of the top-down movement with the initial development of the cluster strategy and its support under the PSEDA conditions. For example, M. Wickham [28] considers the role of the state when creating clusters as the most important and identifies in the totality of factors for the successful role of the government to create conditions favorable for cluster formation, provision of the necessary infrastructure for cluster development and formation of new leading companies. In addition, it was noted [29] that governments (32%), businesses (27%) and jointly by business and government (35%) are the initiators of cluster formation, cluster is financed by the government (54%), business (18%), jointly by business and government (25%).

An important tool for cluster formation based on PSEDA is the financial and economic mechanism that includes an investment mechanism, and, most importantly, a tax mechanism (creating conditions to foster business development).

As a result of research, analysis and systematization of cluster theory, foreign cluster management practice, methodology and practice of cluster policy implementation in Russia and abroad, Russian pilot innovation clusters, problems, constraints and risks of clusters development, main principles to form intra-
regional (municipal) industrial clusters under PSEDA are in single-industry towns are defined:

– when choosing clusters that can develop within the PSEDA mono-town, the concentration of enterprises carrying out profile, related and supporting lines of activity should be assessed, since high value of activity promotes the spread of innovations. This is also important to stimulate domestic competition, especially in the field of innovation that promotes selection of most effective players and re-flow of labor and investment. When choosing the mono-town to support the mono-industry based on PSEDA are the clusters running in industries with economic indicators that are much higher than the average level in the country;

– use of the network strategy to obtain advantages from the ability to coordinate network structures, adapt to changing conditions, quick response to changes in market conditions, specialization, cost reduction;

– creation of attractive conditions for urban environment for the skilled personnel and innovative entrepreneurship to avoid the domination of the city-forming enterprise and to ensure diversification of the urban economy;

– arrangement of specialized managing companies that implement functions of cluster management, including the coordination of the strategies of participants, interaction with governmental authorities to build effective communications within and between the cluster, as well as to improve skills, training, identify areas of cooperation among participants, intensify cross-sectoral interaction;

– use of outsourcing, that is, clustering through cooperation, involvement of multiple independent companies and competition between them around core enterprises, including, for example, city-forming enterprises and large plants. To form clusters - networks of competing suppliers and contractors, research institutes at certain territories, certain conditions are required, and therefore, the practice of transferring individual business processes for outsourcing is important, since it forms the market for many potential cluster members, the existing organizations and start-ups;

– development of internal competitive environment (in this case, we consider the competition not as an antagonistic struggle between the cluster members and the parallel, simultaneous maintenance (and, therefore, duplication) of same functions). Relying on the functional approach to define the competition (that describes the role of competition in the economy), as per J. Schumpeter who describes under his theory of competition economic development as a rivalry between the old and the new, we consider competition as a mechanism that expels entities that operate inefficiently using obsolete technologies. In justifying the need for internal competition, we rely on perception of the competition not as the conflict between the cluster participants, not as the antagonistic form of competition between enterprises and organizations. The competition is deemed as a form of competitiveness between subjects as an element of market mechanism introduced into the system of functioning and cluster development. In this case, we consider the competition as a driving force to increase the efficiency of activities, including innovation, such as the interaction between cluster members, their coexistence, cooperation, and interconnection to increase the competitiveness of the cluster as a whole. Competition in this case is a selective and flexible mechanism. The first is manifested in the fact that enterprises performing ineffectively can be "absorbed" more efficiently. The flexibility of the mechanism of internal competition is shown in its rapid reaction to any changes in the situation. When changes emerge, the entities emerge in the best position capable to quickly adapt to changes. Thus, the competition is the most important mechanism to ensure the cluster effectiveness.

The prospective development of PSEDA-based clusters determines adoption of the strategy by enterprises based on "open innovation" model [21], the application of incoming and outgoing knowledge flows to strengthen innovative processes within companies. It is important to attract third-party solutions as a result of outsourcing, networking, involvement of customers, and also to involve employees in the innovation creation.

The gradual formation of the intra-regional industrial cluster under PSEDA is defined by the sequence of "formation of certain conditions in the mono-town - key enterprises - related organizations". This chain of events in process of cluster formation considers the operation of market mechanisms and stimulates emergence of key firms capable to form the core of the cluster. The most important elements for the effective cluster functioning are the business climate, infrastructure, access to resources, capital markets, taxation system, administrative barriers, transport infrastructure. In this sense, the conditions formed under PSEDA are favorable to identify and form intra-regional (municipal) industrial clusters in single-industry towns. However, when identifying clusters, their ability should be considered to emerge in the course of extensive manifestation of the market mechanism when enterprises seek concentration due to obvious advantages of the geographic location. For example, Porter and Enright believe that clusters should not be formed from scratch, but rather to develop those agglomerated.

Let's consider the gradual cluster formation.

Stage I. Analysis of social and economic state of single-industry town, identification of promising economic agglomerations, identification of cluster formations, assessment of their formation and development potential, selection of projects to create and develop intra-regional (municipal) industrial clusters.

Stage II. In process of organizational design of clusters, it is required to fist consider the needs of participating entities in certain types of targeted interaction that specify the motivation for association: integration of supply, sales, marketing; use of common economically viable suppliers; integration of the unified scientific and technical policy; exchange of work experience and innovations; coordinated actions to retain and expand positions in the market. The
choice of particular spheres of activity is expedient to justify based on analysis of the marketing research results and perspectives for the sales market development.

The Stage III provides: choice of major cluster activities in the strategic perspective; inclusion of structures actively playing at the market, first of all marketing, supply-marketing, design, etc. (allocation of the group of specialized suppliers and service enterprises); development of future common intra-cluster solutions and approaches; development of principles for the management of the enterprise network.

The formation and development of networks (industrial and business) is based on the combination of key competence of the large enterprise, totality of medium-sized enterprises, a number of small firms (auxiliary, service, service enterprises). The autonomy of unincorporated entities to match with clear rules of inter-organizational interaction, initiates the emergence of sustainable synergies in networks.

Features of network structures: stable nature of cooperation, the need for which is specified by the complexity of final product, its growing science-intensive and long-term research and production cycle. The inter-sectoral principle of cooperation is associated with the involvement in technological process of not only production but also marketing (justification of feasibility to create new products and markets for sale thereof), scientific and technical, sales and service (dealers, leasing companies, maintenance centers, recycling, etc.), financial organizations.

The main feature of the network is that technologies, know-how and other intangible assets are produced and sold created by the request of the managing company of this chain. This requires the use of special network forms of organization of the scientific and production cycle. The networks are distinguished by cooperation (joint creation of value, but not just the market exchange) and the special role of internal infrastructure, interpersonal links, and knowledge transfer.

The cluster that includes a managing company and a network of entities as a core, has a number of advantages to structures that act under strict legal frameworks: freedom to "enter" and "exit" from the network and cooperation ties; the most effective cooperative relations are developed and strengthened, the less effective ones easily die off (with no legal problems); unlimited number of participants, arbitrarily "long" chains of interrelations (technological, economic, financial); ability to integrate resources of different number of participants to the structure to invest in projects aimed at creating new and improving production and cooperation; reduction of transaction costs.

The proposed step-by-step mechanism for cluster formation supposes its gradual increase in its boundaries due to inclusion of participants in the production and business networks. Such a mechanism has advantages as follow: first, it avoids miscalculations and mistakes in determining the structure and types of activities within an intraregional (municipal) cluster; second, the functioning in the network will identify problems of interaction, points of contact, promising areas of joint activities, adjustment of characteristics of joint entities, elaboration of interaction principles.

The effectiveness of cluster project implementation is defined by appearance of the cluster features: synergetic effects, stability of intra-cluster material and information flows, system-forming factors, ability to self-organization and self-development, and continuity of functioning. The cluster should be formed with minimal expenditure of resources, but no compromising of the process effectiveness. The voluntary association of members should be encouraged.

Data analysis of social and economic development of the town as shown on the official website of the Yurga Town Administration makes for the conclusion as follows [30].

First, there is an increase in economic performance figures of the mono-industry town in 2011–2012 followed by the abrupt negative trend in 2013 with some recovery in 2014. Against the overall favorable macroeconomic situation in 2011, there was the upward trend in the economic development. The physical index of industrial production was 122% (12.1 bln rubles), the volume of commodity turnover was 7 bln rubles. The physical index of industrial production in 2012 amounted to 103.2% (13.6 bln rubles). The sales volume reached 7.7 bln rubles (physical volume index is 100.4%). However, yet in 2013, the economic development figures grew to have the negative trend. The index of industrial production in 2013 reduced to 75.6%, and the sales volume – to 75.2%. By the end of 2014, this figure reached 96.6% (see table 1). The transition of the positive trend to negative is reported in the volume of industrial production in the town, especially for manufacturing entities (Table 1) [30], whereas this figure slightly changes for the production and distribution of electricity for the studied period.

Second, the structure of industrial output changed by types of economic activity within 2011–2014. The share of manufacturing entity slightly reduced as follows: from 87.85% in 2011 to 84.24% in 2014. Whereby, the reduction in the volume of shipped products was reported for metallurgical products (by 14% in 2011-2014 from 4186 to 3681.9 mln rubles) and machinery and equipment production (26% growth in 2012 against the previous year and the overall reduction by 84% in 2011 to 2014 from 3,218 to 510.1 mln rubles), while the production of non-metallic mineral products showed an increase by 51% in 2011-2014 (from 1912 to 2893.9 mln rubles) (See Figure 1) [30]. The latter occurs during the construction material industry development in Yurga. The change in the investment pattern to fixed assets of the town also results in the change in the structure of industrial output volume.
Table 1. Changes in industrial output of municipal formation “Yurginsky Municipal District”

<table>
<thead>
<tr>
<th>No</th>
<th>Types of economic activity</th>
<th>2011</th>
<th>2012</th>
<th>By 2011, in %</th>
<th>2013</th>
<th>By 2012, in %</th>
<th>2014</th>
<th>By 2013, in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Volume of industrial output of the town, mln rubles including for large and medium-sized enterprises</td>
<td>12401</td>
<td>13593</td>
<td>110.2</td>
<td>10662</td>
<td>78.4</td>
<td>11331</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1717</td>
<td>12907</td>
<td>109.6</td>
<td>9924</td>
<td>76.9</td>
<td>10657</td>
<td>107</td>
</tr>
<tr>
<td>2</td>
<td>Manufacturing entities, mln rubles including large and medium-sized enterprises</td>
<td>10751</td>
<td>11944</td>
<td>111</td>
<td>9018</td>
<td>75.5</td>
<td>9632</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10071</td>
<td>11263</td>
<td>111.8</td>
<td>8281</td>
<td>73.5</td>
<td>8977</td>
<td>109</td>
</tr>
<tr>
<td>3</td>
<td>Production and distribution of energy, gas and water, mln rubles including large and medium-sized enterprises</td>
<td>1650</td>
<td>1649</td>
<td>99.9</td>
<td>1643</td>
<td>99.7</td>
<td>1696</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1646</td>
<td>1644</td>
<td>99.9</td>
<td>1643</td>
<td>99.9</td>
<td>1680</td>
<td>102</td>
</tr>
</tbody>
</table>

Fig. 1. Changes in the volume of shipped products to manufacturing entities for 2011–2014 (mln rubles).

Third, the structure of real investments has changed: investments in buildings and structures in 2011–2014 significantly increased. The implementation of the Integrated Investment Plan for Upgrading reasonably involves a change in the structure of investments. During the period from 2011 to 2014, the ratio of investments in buildings and structures radically changed (share in 2014 was over 60% against slightly over 30% in 2011) and in machinery, equipment, vehicles and tools (reduction in share from 64% to 35.1% over the same period) (Fig. 2) [30].

Fourth, the structure of investments changed by the types of economic activity towards the reduction in metallurgical products and growth in wholesale and retail trade, repair of vehicles and motorcycles, production of household goods and personal consumables in 2011–2014. [30]. Exemplary is the change in the structure of investment by the types of economic activity. If in 2011 the equity contribution to the capital stock of metallurgical production and production of finished metal products amounted to 62.7% of total investments, by 2014 it declined to 11.02%. Whereas, the equity contribution to capital stock in wholesale and retail trade and repair of motor vehicles and motorcycles, household products and personal consumables increased from 2.4% in 2011 to 47.3% in 2014, the latter figure is the resultant of obvious trends to diversify the economy of the town. These changes cause alterations in the structure of industrial production, reducing the share of city-forming enterprises of a mono-industry town (Fig. 3) [30].
Fig. 2. Trends in changes in the structure of investments by types of fixed assets in 2011–2014.

The share of town-forming entities is reduced in the total volume of shipped products from 51.2% in 2011 to 12.3% in 2014. Thus, the industrial production index in 2013 was 75.6%, increasing to 96.6% by 2014. Moreover, the cumulative problems of city-forming entities affected the share reduction therein resulting in the natural decrease in the volume of shipped products and industrial production index of the mono-industry from 90.9% in 2011 to 38.2% in 2014.

In 2011, 9 projects were among projects to create and invest in small enterprises (4 of them were suspended) raising investments from extra-budgetary sources in the amount of 171 mln rubles that made it possible to create 248 new jobs. By 2012, the small business investment projects amounted to 6 with 271.94 million rubles raised and 93 jobs created. However, in 2013 the number of small business projects decreased to 4, and in 2014 – to 3. The joint investments to implementation of these projects in 2013 amounted to 264 mln rubles, in 2014 – only 24 mln rubles, while 218 and 42 work places were created, respectively. At the same time, the volume of extra-budgetary funds to finance projects significantly reduced in 2014 against the figure in previous years.

It should be noted that the share reduction of the Limited Liability Company "Yurginsky Machine Building Plant" in the municipal industrial output does not result in the decrease in the company impact on the mono-town standing to diversify its economy. So, if in 2011–2012 the company succeeded to implemented a range of measures to upgrade, reconstruct and retrofit the entity, introduce up-to-date technologies and equipment at the expense of 350 million rubles allocated, in 2013 the position of the largest system-forming enterprise impeded. That was resulting from macroeconomic deterioration, decrease in consumption...
level and coal prices that caused a reduction in investment projects of coal mining companies to acquire the equipment. In this connection, the volume of commodity output of the plant reduced by 50%, and the average monthly salary – by 25%. During 2013–2014, the number of employees decreased by more than 1,700 persons (up to 3959 persons). The resulting state gave rise to the introduction of extreme situation at the Yurginskaya CHP on the balance of Yurginsky Machine Building Plant LLC. These circumstances make for the conclusion to reduce the share of the enterprise in the volume of municipal commodity output, number of labor force employed in the core enterprise under conditions where the performance of the enterprise highly impacted the social and economic state of the town. The latter circumstance evidence on negligible changes in the dependence on the enterprise activity and mono-profile capacity in case of formal reduction in the mono-town criteria parameters. This conclusion is proposed based on the need to consider both the official level of the mono-town criteria to assess its economy diversification and the reduction in the influence of the city-forming (backbone) enterprise to the municipal economy [30].

Although the economy of the monogorod Yurga over the period 2011-2014 has changed towards a greater variety of economic activities, this was not only due to implementation of modernization program for the mono-industry town, but largely due to a sharp decline in the share of the city-forming enterprise in the mono-industry economy. Such reduction is associated with scheduled measures to restructure the municipal economy as a whole as per the comprehensive plan and with consequences of negative macroeconomic factors.

The existing agglomerations were reviewed to identify cluster entities in Jurga: machine-building, agro-industrial and complex production of building materials. Let's consider the factor assessment in detail that contribute to the creation of agro-industrial cluster.

Apart from Kuznetsk Office Ferroplavky JSC, Yurginski Ferroplavky Zavod stand-alone business unit, ZavodTekhnoNikol-Sibir LLC, Komus-upakovka Siberian Plant, among the largest industrial enterprises of the town there Kuzbasxkhleb LLC, bakery plant No. 3 in Yurga, “Yurginskiy Gormolzavod” JSC. About 500 small businesses are registered to run in Yurga, 75 of them are engaged in manufacturing industries. In recent years, the distinctive feature in development trends of small business in the town is its production trend.

The SWOT analysis of social and economic conditions in Jurga afford focusing on the following competitive advantages. In terms of geographical location and climatic conditions, these include the density of town location, the proximity to the regional center and major cities of the Siberian region, namely Novosibirsk and Tomsk (intersection of three highways), transport communication support (road, water, railway), location of the West Siberian landfill near the town, the consumer of goods and services of Yurga manufacturkers, the supplier of labor force to the town (officers' wives, persons demobilized in reserves from military forces), the factor contributing to social stability in Yurga, strengthening links with federal and regional authorities. In view of demographic potential, the standard of population living and the labor market, it includes an increase in the birth rate since 1997, the reduction in infant mortality rate, in general mortality rate and availability of free man power. As for engineering infrastructure and accommodation, the population in the town is provided with utility services, engineering and transport infrastructure, the housing construction rate doubled since 2000. As for the environmental situation, it covers free and vast lands for the development of agroindustrial cluster and assumes low susceptibility to natural disasters. Along with machine industry and production of building materials, food industry is noted among main industries. Besides, the territorial proximity of the town and the region favorable for agriculture and livestock production allowing supply of agricultural products to the town both for population needs and to food production plants. Among competitive advantages are the following: availability of vocational schools, technical schools, university branches that ensure the adequate number of qualified personnel, the infrastructure for entrepreneurship support available, availability of four manufacturing sites suitable for the construction of various facilities. The city has the advanced infrastructure available in the dense location of the town with the adequate land plots, buildings, facilities available for investment purposes. Geographic and transport availability favorable for investors should be highlighted. There are sufficient land resources for agricultural, industrial and other purposes within the agro-industrial cluster to study.

The known favorable factors include the convenient geographical location of the town (mid location between the regional centers of the Siberian Federal District, namely Kemerovo, Tomsk and Novosibirsk cities, availability of railway communication, good proximity of underground oil and gas mains, high-voltage transmission lines, arrangement of the town on the bank of the Tom River which is the main waterway for the Kemerovo region). The competitive advantages of the town include: the developed system of professional education (Yurga Institute of Technology of the National Research Tomsk Polytechnic University,three colleges (The Yurga Technical College of Machine Industry and Information Technologies, the Yurga Technical School of Agrotechnology and Service, the Yurga College of Technology)), high rate of population with higher and secondary technical education, availability of qualified specialist engineers from the city-forming enterprise (machine-building plant), free investment sites of 549.4 hectares in area and the engineering infrastructure.

As of January 1, 2016, the share of permanent residents in the town amounts to 80484 people, 43214 people are employable population in productive age, 760 people are engaged in the production of food products, including drinks and tobacco goods. In 2014
and 2015, the agricultural output is rated in the amount of over 230 thousand rubles, in 2014 the volume of own-produced goods shipped, delivery of works and services on their own (with no small business involvement) amounted to 12,490.00 thousand rubles, and in 2015 - 514,683.7 thousand rubles.

The agro-industrial cluster will consolidate the greenhouseing, the dairy plant, the industrial company for production of beverages and mineral waters "YUSIL", the bakery complex, the greenhouse plant of 5 hectares in area. By 2020, the following is scheduled: implementation of projects to establish a plant for the rainbow trout production of more than a thousand tons per year in volume and fish production recycling (Sibirskaya ryba LLC), expansion of the greenhouse complex (Zeleniy proekt LLC) up to the area of 20 hectares. The cost of projects totals 2165 million rubles. 710 new jobs will be created. In particular, the establishment of the fish-breeding complex for commodity cultivation of rainbow trout will make it possible to saturate the market of the Kemerovo region and other regions with refrigerated and fresh fish products, since production of more than 1,000 tons per year is expected. Peculiarities of cluster strategy implementation and the possibility to create the agricultural complex in Yurga as the standard mono-town of the Kemerovo region is not only PSEDA-based benefits (tax privileges and preferences), but is also based on the identified competitiveness of products bred directly in the region, due to proximity to the consumer, among other things. Public catering establishments and retail chains of Siberian regions compose the target group of consumers. In addition, the higher competitiveness, for example, of trout, will be supported by processing options (smoking, canning, etc.), free delivery management of large batches within Kemerovo, Tomsk, Novosibirsk cities (convenient geography point usage), commercials (brand development and promotion). The consumer similarity is rated as the competitive benefit.

Analysis of figures to identify the agro-industrial cluster, physical output indicators of agricultural and food products, volume of investment in the development of agro-industrial enterprises, as well as opportunities and competitive advantages that ensure investment attraction, the growth of business concern in arrangement of entities and production facilities in the PSEDA of Yurga prove on the high potential to create and develop the agro-industrial cluster in the mono-town.

The following is deemed as positive results of cluster formation in Yurga (predicted by municipal authorities of Yurga): increase in the number of taxpayers and taxable base; emergence of the convenient tool for interaction between large businesses and small and medium-sized businesses; the municipal budget revenue increase; diversification of the economy, use of excess capacity and the territory of the former city-forming enterprise (Table 2).

Among the deterrent factors in Yurga the following may be distinguished: poor quality of business environment (prior to PSEDA), poor development of business associations (chambers of commerce, industry associations) that often fail to achieve the productivity goals and promotion of priorities and interests of the regional business.

As per estimation, the use of cluster approach to form the PSEDA program in Yurga the best effective clusters are identified for the territory. However, it is important to identify the best effective clusters for single-industry towns and establish a specialized entity in a mono-town that executes the cluster management.

PSEDA-based cluster formation contributes to occurrence of synergistic effects, in particular, technological effects due to the spread of technological innovations, resources and infrastructure based on joint use of key resources and PSEDA infrastructure on preferred terms.

Table 2. Estimated figures of cluster formation under PSEDA in the mono-industry town of Yurga, Kemerovo region

<table>
<thead>
<tr>
<th>Figure</th>
<th>Without PSEDA</th>
<th>With PSEDA (in the first five years)</th>
<th>If there are clusters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of enterprises, units</td>
<td>2839</td>
<td>2889</td>
<td>Over 3000</td>
</tr>
<tr>
<td>Labor force, pcs</td>
<td>35 600</td>
<td>38 100</td>
<td>40 000</td>
</tr>
<tr>
<td>PIT allocations to the municipal budget, rubles</td>
<td>574 609 000</td>
<td>945 208 000</td>
<td>1 172 057920</td>
</tr>
<tr>
<td>Insurance contributions from the wage fund, rubles</td>
<td>1 334 860 907</td>
<td>567 124 799</td>
<td>431 014 847</td>
</tr>
<tr>
<td>Budget revenues, rubles</td>
<td>912 464 200</td>
<td>1 465 377 000</td>
<td>1 817 067480</td>
</tr>
<tr>
<td>Debts of municipal budget, rubles</td>
<td>183 122 000</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
CONCLUSION

The PSEDA-based intraregional (municipal) industrial cluster in the mono-town is proposed to consider as the tool to deploy the industry and its network, association of entities to implement projects to diversify the mono-town economy and investment projects meeting the PSEDA requirements. It is indicated, either, that the intraregional (municipal) industrial cluster is the special type (category) of the territorial cluster, regional industrial cluster and the industrial district. In addition, the features distinguishing the intraregional (municipal) industrial cluster from other types are systematized. It is validated that the scenario approach is required to creation of PSEDA municipal clusters based on the priority of from top downward movement with the initial development of the cluster strategy and its support under PSEDA conditions. Basic principles are specified to form the intraregional (municipal) industrial clusters when creating PSEDA in monotowns that differ from those combination in practice: priority evaluation criteria when choosing clusters with the capacity to develop under the mono-industry town PSEDA; phased networking; use of PSEDA options to create the favorable urban environment; harmonization of participants' strategies; use of outsourcing; development of internal competitive environment as a form of competitiveness of subjects and the market mechanism element integrated into the system of cluster functioning and development. The stages of cluster formation are proposed assuming identification of perspective economic agglomerations, identification and assessment of the cluster formation potential; arrangement of cluster design in view of needs of participants in certain targeted interaction; the choice of basic fields of concern of the cluster in strategic outlook. The staged mechanism for cluster formation assumes a gradual expansion of its boundaries by including participants of manufacturing and business networks. The advantages of the staged mechanism are distinguished to form the cluster. This makes to minimize mistakes when determining the composition and kinds of activities within an intraregional (municipal) cluster, coping with interaction problem. The results of this method evaluation are reviewed with specific reference of cluster formation for PSEDA-based mono-town Yurga. In particular, by the results of analysis of figures obtained for agro-industrial cluster identification and opportunities and competitive benefits of the territory, the high potential is concluded to create and develop the agro-industrial cluster in the mono-town.

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REFERENCES


CATERING SERVICE AND ITS QUALITY FOR UNIVERSITY STUDENTS IN MUNICIPAL FORMATION

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Abstract: More and more works are published in scientific literature, concerning the study of students' health and the factors, influencing it, the most important role among which is devoted to rational nutrition. Scientists proved that students' special life style, age-specific peculiarities, intense intellectual and physical activity, irregular studying schedule, lack of money, personal disorderliness and other conditions of students' life demand for special attention to the arrangement of their nutrition. The results of sociological researches, conducted among the Russian students (in Kemerovo and the Kemerovo State University) demonstrate quite a critical relation of students to the quality and functioning of catering service at universities and to price availability of meals in canteens. The analysis of foreign and Russian experience of healthy catering service for students leads to the conclusion that students' centralized nutrition in municipal formation needs to be arranged according to the mechanisms, regulated by the federal program “Shkol'noe pitanie” [School nutrition]. The offered project of the city research and production complex for production of ready meals and semi-finished products for university canteens will allow to increase the students' nutrition quality, improve their health, provide cost efficiency of university public catering, create new workplaces in the city, involve local producers in foodstuffs procurement, develop and implement special programs for students etc.

Keywords: Nutrition, students, health, morbidity, quality of food, canteen, food habits, catering service, municipality


INTRODUCTION

According to the Law “Ob obrazovании в Rossiyskoy Federatsii” [On Education in the Russian Federation] (article 28, clause 15) creation of necessary conditions for preservation and strengthening of health of and catering service for students and employees of educational organizations is established for educational organizations (Federal Law dated as of 29.12.2012 No. 273-FZ (reviewed on 02.03.2016) " Ob obrazovании в Rossiyskoy Federatsii” [On Education in the Russian Federation]). Despite the fact that nutrition is not the main activity of educational organizations, normal study and upbringing processes are impossible without it, including at universities. Therefore, nutrition quality issues and its effective arrangement at universities should be paid much attention to by management and public organization of university on the one hand, and by scientists on the other.

The issue of students' nutrition is cross-disciplinary. Medics, biologists, ecologists and hygienists consider the issues of rational nutrition, its element-by-element content, calorie content, influence on health and safety. Specialists in the field of foodstuffs production and recycling and in the field of cooking methods study nutrition technological aspects. Sociologists and psychologists study consumer behaviour, stereotypes, nutrition culture and relation to healthy nutrition and pernicious food habits. Topics, dealing with qualitative nutrition arrangement, price policy, cost efficiency of student canteens operation, cafes and buffets belong to economic and administrative science.

Attention to students' nutrition in Russia has been paid to for a long time - even at the end of the 19th century the Russian Society of Public Health Safety offered to arrange "normal canteens" in Moscow and Saint-Petersburg for the studying youth, where nutrition would be based on physiological standards [1]. The results of many researches of the latest decades show that the issues of students' nutrition and its arrangement are relevant and require a serious consideration. Thus, the most frequent nutritional disorders of students, revealed in researches of the 1990s, were irregularity (36%) and dry eating (31%). This resulted either in weight loss (41%), or in overweight, which was found in 9% of students. In surveys students of that time mentioned a sharp increase in food prices at its low quality. Student public catering was becoming unavailable for more than a half [2].
Modern researches (I. P. Balykova et al. [3], E. A. Goreva et al. [4], N. A. Drozhzhina et al. [5], N. N. Zarubina [6], S. A. Krylatov [7], A. V. Noskova [8], Zh. V. Puzanova et al. [9], S. I. Samygin et al. [10], N. V. Semenova et al. [11]) underline preservation of tendencies of nutrition disorder among university students, but nowadays, they are added by rare eating of hot meals and appearance of new food habits – eating a lot of fast food, high-fat, refined products, chips, instant food and drinking a lot of carbonated drinks, made on the basis of chemicals.

Researchers refer lack of money, intensity of studying and lack of attention to their own health to the reasons, causing balance and nutrition disorders of students. They think that high prices and low quality in student canteens together with economy in nutrition leads inevitably to health disorder [12]. It is not surprising that digestive organs diseases have a high position in the structure of morbidity and chronic diseases.

Sector of health social problems of the Institute of Sociology of the Russian Academy of Sciences conducted annually from 2001 till 2008 a monitoring Moscow Students’ Health (2363 respondents); according to its results, negative dynamics of students’ morbidity are registered. It became clear that the most spread diseases are gastrointestinal (gastritis, colitis), pulmonary and cardiovascular. The monitoring data also revealed a persistent growth in the number of Moscow students with chronic diseases, their number increased by 10% during the observance period. It is stated that there are more junior and senior students among them, then freshmen and sophomores. Researches point out the existence of interdependence between chronic afflictions among students and their level of prosperity. In the low-income group every second person has some chronic disease, in the average-income group each third respondent has it [13].

Foreign scientists [14, 15, 16, 17] also pay much attention to the issues of nutrition of student youth. Their research results should be taken into account, developing the ways of improvement of food quality and nutrition arrangement for students in Russia.

Brief review of the problem under consideration shows that non-standard approach is needed for a significant breakthrough in university catering service. This approach should firstly be based on the best practices of catering service for students and secondly should take into account the specific feature of the territory (region, municipal formation), on which a university (institutions) is located.

The objective of the present paper is to justify the necessity of improvement of catering service for students of universities of a municipal formation (by the example of Kemerovo) to improve quality of their nutrition and to offer a corresponding variant.

**OBJECTS AND METHODS OF STUDY**

The object of the present research is university students in Kemerovo; the subject is quality and arrangement of their nutrition in educational organizations.

62109 people are studying at universities of Kemerovo Oblast'. Most of students are part-time ones – 30638 people, 29903 people are full-time students and 1668 people are full-and-part-time students (according to the data of October, 2015). The greatest university is the Kemerovo State University, 17289 students are studying at it, including 9164 people, studying at the branches.

There are several universities in Kemerovo: Kemerovo State University (main university – 8125 people), Kuzbass State Technical University (main university – 7339 people), Kemerovo Institute of Food Science and Technology (5265 people), Kemerovo State Medical Academy (3215 people), Kemerovo State Agricultural Institute (2994 people), Kemerovo State Institute of Culture (2821 people), branches of educational organizations in other regions (3651 people). The total number of students at Kemerovo universities is 33410 people or 6% of the city population.

The specific features of studentship are: age-related characteristic from 17 to 25 years old; specificity of educational activity (intellectual nature of labour, regulated by the university curriculum, specific resting time rules), income structure (scholarship, parents' aid, individual earning). The obvious significant feature of this group, which draws attention of researchers, is student age. Thus, it is stated that this period is the most important for formation of personal position, establishment of a wide range of social relations, exploration of the future professional activity, adoption of new behavioural norms and orientation to the desired social roles [18]. Herewith, the researchers do not have a unified position on the essence of the definition of student age. A famous sociologist I. S. Kon analysed the specific features of the student age and pointed out the priority of a social aspect. That is because time boundaries of studentship clash with the period of adolescent age which is complex and contradictory but significant for the social maturity of an individual [19, 20]. M. Ya. Vilenksiy and S. O. Avcihinnikova point out the priority of psychophysiological aspect, analysing the student age. They characterise it as a period of peaks of organism physiological potentials [21].

Studying studentship, other aspects are also highlighted, associated with the difficulty of studying at a university. They are organizational conditions and organism psychophysiological peculiarities (V. V. Zashikhina et al. [22], O. F. Kushnerova et al. [23], E. M. Kharlanova [24] etc. [25]).

As it has been stated earlier, one of the incomes (and often the main one) of a student during his/her studying is scholarship. At state universities students are assigned a state academic scholarship, which differentiates, in particular, depending on the location of an educational organization. For example, the minimum size of the state academic scholarship for students of the Kemerovo State University, who have passed exams with good and excellent marks, is 1930 rubles per month and for the students who have only excellent marks it is 2895 rubles (the Russian Federation Government Decree dated as of...

Students, studying at the expense of budget funds and who needs social aid, upon presentation of supporting documents, are assigned a state social scholarship of 2895 rubles per month, students, passing the exams with good and excellent marks, have a scholarship of 4824 rubles, with excellent marks – 5789 rubles.

Mandatory payees of social scholarship in accordance with the law are children-orphans, disabled people of the 1st and the 2nd groups, liquidators of the Chernobyl accident, combat disabled people and veterans.

Senior students may be assigned an enhanced state scholarship if they have good and excellent marks, conduct active scientific-research, cultural and creative, sport and public activity and have achievements in studying. The scholarship size is determined by the University Academic Senate, involving representatives of student government.

In certain cases, freshmen and sophomores in need may also be assigned such a scholarship. Its size for students with excellent marks is 9965 rubles, with good and excellent marks – 9000 rubles (Russian Federation Government Decree dated as of 2nd July, 2012 No. 679 “O povyshenii stipendiy nuzhdayushchimsya studentam pervogo i vtorogo kursov federal'nykh gosudarstvennykh obrazovatel'nykh uchrezhdeniy vyshego professional'nogo obrazovaniya, obuchayushchikhsya po ochnoy forme obucheniya za schet byudzhetnykh assignovaniy federal'nogo byudzheta po programmam bakalavrata i programmam podgotovki spetsialista i imeyushchim otsenki uspеваemosti “khorosho” i “otlichno” [“On enhancement of scholarship for full-time freshmen and sophomores in federal state educational institutions of higher professional education, who study bachelor or specialist learning programs at the expense of budgetary funds of the federal budget and who have good and excellent marks”]). URL: http://base.garant.ru/70196772/.

Financial support may be paid to students as a financial aid. Full-time students of the vulnerable category (orphans, disabled people, students from a large family, low-income students) may be provided with a food package.

Students-orphans or students who lost their parents have the right for full state support which presupposes free nutrition or refund for it (from 2014 it is 260 rubles for a working day and 286 rubles for a day off or a calendar day), provision of clothing kit or inventory (or refund of their price according to the norms), right for free accommodation in a dormitory and for free medical care during the whole period of studying (Federal Law "O dopolnitel'nykh garantiyakh po sotsial'noy podderzhke detey-sirot i detey, ostavshikhsya bez popecheniya roditeley" [“On additional guarantees of social support for children-orphans and children, lost their parents”], dated as of 21st December, 1996 No. 159-FZ). URL: http://base.garant.ru/10135206/; (Russian Federation Government Decree dated as of 7th November, 2005 No. 659 “Ob utverzhdenii norm material'nogo obespecheniya detey-sirot i detey, ostavshikhsya bez popecheniya roditeley, obuchayushchikhsya i vospityvayushchikhsya v federal'nykh gosudarstvennykh obrazovatel'nykh uchrezhdeniyakh, nesovershennoletnikh, obuchayushchikhsya i vospityvayushchikhsya v federal'nykh gosudarstvennykh obrazovatel'nykh uchrezhdeniyakh – spetsial'nykh professional'nikh uchilisheakh otkrytogo i zakrytogo tipa i federal'nom gosudarstvennom uchrezhdenii “Sergievo Posadsky detskiy dom sloeglukhikh Federal'nogo agentstva po zdравookhraneniyu i sotsial'nomu razvitiyu” [“On approval of norms of financial support for children-orphans and children who lost their parents, persons from among children-orphans and children who lost their parents, who study and are brought up at federal state educational institutions, of persons who have not reached the age of majority, who study and are brought up at federal state educational institutions - open- and closed-type special professional schools and at the federal state institution Sergiev Posad boarding school for children with blindness and deafness of the Federal Agency on healthcare and social development”]). URL: http://base.garant.ru/188814/.

To justify the necessity of improvement of approaches to student catering service, the following methods were used in the present research as the main research methods: analysis of statistics, official documents and other materials; secondary analysis of sociological researches results; comparison and analogy. For a deeper study of catering service system at Kemerovo universities, the Kemerovo State university experience was additionally analysed (results of several representational for the university sociological researches).

RESULTS AND DISCUSSION

In the current context, students experience greater burden at conscientious attitude to learning. The study process requires memory exertion, attention concentration, is often accompanied by stressful situations associated with exams, tests and intermediate control. The consequences of students' mental strain in combination with reduced physical activity may be health deterioration, working capacity decrease and decrease in resistance to various diseases. The process of adaptation to the new social conditions, associated with studying at a university, may cause depletion of body physical reserves, especially during the first semesters [26, 27]. All this requires from students the observance of a healthy lifestyle and, first of all, of healthy nutrition principles.

However, definitive conditions for a healthy nutrition, which meets the requirements of normal functioning of a young organism, have not been created.
yet, which is proved by the data of the sociological research "Kuzbass Student", conducted in 2013 in Kemerovo Oblast’ by the sociological laboratory of the Kemerovo State University by the decision of Expert Advisory Body of the region universities on monitoring of attitude of educational process subjects to socially significant events, which covered 2973 students of the 9 universities of the federation subject. Let’s refer to the data, obtained during this research, on Kemerovo universities as a whole (2444 students of 7 universities) and on the biggest university in the region – the Kemerovo State University (566 students have been questioned).

Defining the most relevant problems of students, respondents have been offered to assess quite a wide range of these problems (21 items), from which one could select up to 6 variants. The data indicate that students of different universities have ranged their difficulties differently, but the lack of money for food appeared to be in the top of ten most significant problems – at the Kemerovo State University 16% pointed out this problem, at other Kemerovo universities – 17%. Data comparative analysis results, depending on social and demographic characteristics, showed that at the Kemerovo State University and at Kemerovo universities totally this problem disturbs, first of all, low-income students, studying on a budgetary basis and living in university dormitories.

In the course of the research under consideration the respondents were questioned about the expenditures which are most relevant for students in terms of financial support (the respondents were offered a list of financial costs, specific for studentship) (see Table 1). The question presupposed the possibility of choosing several answers (up to three), therefore, the sum of percentage in each column exceeds 100%.

Judging by the obtained answers, expenditures for food are the most problematic item of expenditures for the majority of students; 59% of respondents at the Kemerovo State University and 58% of respondents at other Kemerovo universities specified it. Comparison of data on socio-demographic characteristics showed that this measure is more important for freshmen living in dormitories, students studying on a budgetary basis and low-income students.

The represented sociological data on Kemerovo demonstrated the relevance of student qualitative catering service arrangement. But the results of researches, conducted in different years at the Kemerovo State University, allow to make a more detailed justification of the analyzed problem.

Thus, according to the data of representational sociological surveys, dealing with health problems and conducted among the Kemerovo State University students (the researches have been conducted by the sociological laboratory of the Kemerovo State University among students of first to fourth courses of all faculties in April-May, 2012 (covered 1066 respondents) and March-April, 2011 (covered 1096 respondents)) [28], only each forth-fifth respondent kept healthy nutrition to enhance health (see Table 2), they put this measure on a third place after taking vitamins and dietary supplements (55–59%) and sports activity (41–46%).

As well, the results of this research showed that irrational nutrition together with irrational schedule were the main reasons for suffered diseases during the study at the Kemerovo State University (see Table 3).

Moreover, the digestive system diseases are in the second place by frequency among the list of diseases which students suffered during the years of study at university, they have been noted by a quarter of respondents (see Table 4).

**Table 1.** Material expenditures, most relevant for financial support (% from the number of respondents)

<table>
<thead>
<tr>
<th>Answers</th>
<th>Kemerovo State University</th>
<th>other universities of Kemerovo</th>
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<tbody>
<tr>
<td>no such expenditures</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>expenditures for food</td>
<td>59</td>
<td>58</td>
</tr>
<tr>
<td>expenditures for public transport</td>
<td>39</td>
<td>42</td>
</tr>
<tr>
<td>expenditures for getting to a place for students living outside the city</td>
<td>36</td>
<td>32</td>
</tr>
<tr>
<td>accommodation expenditures</td>
<td>33</td>
<td>27</td>
</tr>
<tr>
<td>expenditures for treatment and disease prevention</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>expenditures for the Internet</td>
<td>23</td>
<td>20</td>
</tr>
<tr>
<td>expenditures for cultural events</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>expenditures for study materials</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>expenditures for scientific-research activity</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>other expenditures</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>no answer</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>
It should be mentioned, that less than a quarter of respondents (23–24%) considered their nutrition as rational and balanced. More than a half of respondents (54–57%) claimed that they have malnutrition. There are problems also with nutrition regularity: only a third part of students (33–35%) ate regularly during a studying day; approximately the same number (28–36%) ate irregularly; and approximately the same part (31–37%) ate on different days differently.

The represented data obviously prove the necessity of arrangement of effective operation of catering outlets at universities. The opinion of students and lecturers of the biggest university in Kemerovo Oblast’ on the functioning of these outlets was studied repeatedly.

The results of sociological research, conducted at the Kemerovo State University in 2012–2013 academic years among the students and teaching staff (2294 of students from a freshman to a senior and 567 lecturers of all faculties took part in a questionnaire survey) showed that only each second lecturer and a little bit more than a half of students (56%) think that there are quite enough or rather enough catering outlets at the university, 41 and 42% of respondents respectively think opposite.

Upon the whole, the negative dynamics are observed concerning the issue of sufficiency of catering outlets at the university - in the course of the 9-year monitoring research University [29] the number of positive answers is decreasing (see Table 5).

<table>
<thead>
<tr>
<th>Year</th>
<th>2000</th>
<th>2003</th>
<th>2006</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Assessment by students</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>enough</td>
<td>47</td>
<td>41</td>
<td>32</td>
<td>28</td>
</tr>
<tr>
<td>quite enough</td>
<td>38</td>
<td>38</td>
<td>37</td>
<td>38</td>
</tr>
<tr>
<td>rather not enough</td>
<td>10</td>
<td>14</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td>extremely not enough</td>
<td>4</td>
<td>6</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td>failed to assess</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>total at the university</strong></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>Assessment by lecturers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>enough</td>
<td>33</td>
<td>39</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>quite enough</td>
<td>50</td>
<td>42</td>
<td>49</td>
<td>43</td>
</tr>
<tr>
<td>rather not enough</td>
<td>9</td>
<td>13</td>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>extremely not enough</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>failed to assess</td>
<td>7</td>
<td>5</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td><strong>total at the university</strong></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

According to the research data of 2012–2013 academic years, one-third of students used the Kemerovo State University canteen service several times in a week; other one-third part used it every day.

The rest of respondents use the university catering service rarely (they are 18%) or those who did not visit canteens (16%). Thus, nutrition of each third student

**Table 2.** Forms of enhancing personal students’ health, 2011, 2012 (% from the number of respondents)

<table>
<thead>
<tr>
<th>Forms of enhancing health</th>
<th>2011</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Take vitamins, dietary supplements, herbs</td>
<td>55</td>
<td>59</td>
</tr>
<tr>
<td>Do sports</td>
<td>41</td>
<td>46</td>
</tr>
<tr>
<td>Keep healthy nutrition</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>Do exercises, harden</td>
<td>15</td>
<td>21</td>
</tr>
<tr>
<td>Do not enhance health</td>
<td>18</td>
<td>11</td>
</tr>
<tr>
<td>Are constantly followed up by a doctor, are treated as outpatients</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>Are treated as inpatients periodically</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Are treated in sanatoriums, preventative clinics etc.</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Travel to the sea during holidays</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>Take massage or physiological treatment courses periodically</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Visit quacks</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Other forms</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

**Table 3.** Reasons for suffered diseases, 2012

<table>
<thead>
<tr>
<th>Reasons</th>
<th>% from the number of respondents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irrational nutrition</td>
<td>37</td>
</tr>
<tr>
<td>Irrational schedule</td>
<td>37</td>
</tr>
<tr>
<td>Intensity of exams</td>
<td>29</td>
</tr>
<tr>
<td>Heavy academic load</td>
<td>29</td>
</tr>
<tr>
<td>Careless attitude to the own health</td>
<td>25</td>
</tr>
<tr>
<td>Unfavourable accommodation conditions</td>
<td>14</td>
</tr>
<tr>
<td>Genetic predisposition</td>
<td>14</td>
</tr>
<tr>
<td>Insufficient physical activity</td>
<td>11</td>
</tr>
<tr>
<td>Unfavourable studying conditions</td>
<td>10</td>
</tr>
<tr>
<td>Pernicious habits</td>
<td>6</td>
</tr>
<tr>
<td>Frequent conflicts in a family</td>
<td>2</td>
</tr>
<tr>
<td>Frequent conflicts in a group</td>
<td>1</td>
</tr>
<tr>
<td>Other</td>
<td>4</td>
</tr>
<tr>
<td>No answer</td>
<td>7</td>
</tr>
</tbody>
</table>

**Table 4.** Diseases, suffered by students during the study at university, 2012

<table>
<thead>
<tr>
<th>Diseases</th>
<th>% from the number of respondents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infectious diseases</td>
<td>39</td>
</tr>
<tr>
<td>Digestive system diseases</td>
<td>24</td>
</tr>
<tr>
<td>Eye diseases</td>
<td>20</td>
</tr>
<tr>
<td>Traumas</td>
<td>18</td>
</tr>
<tr>
<td>Nervous system diseases</td>
<td>17</td>
</tr>
<tr>
<td>Genitourinary system diseases</td>
<td>10</td>
</tr>
<tr>
<td>Respiratory system diseases</td>
<td>11</td>
</tr>
<tr>
<td>Heart and vascular diseases</td>
<td>9</td>
</tr>
<tr>
<td>Ear diseases</td>
<td>6</td>
</tr>
<tr>
<td>Other diseases</td>
<td>4</td>
</tr>
<tr>
<td>No diseases</td>
<td>25</td>
</tr>
</tbody>
</table>
may be considered a relatively healthy, moreover, according to the data of observation over consumer preferences, students choose meat and fish meals more seldom and cheaper salads, garnish, soups and baking - more often. Lecturers visit canteens more seldom than students – 36% of them have never used its service.

Fig. 1 indicates assessments by students and lecturers of different aspects of canteen operation. The obtained assessments are higher than the theoretical average one (3.0 points), but lower than a "good" level. The highest assessments were given to the food quality and personnel work, price availability got the lowest assessment. On the average, the canteen operation was assessed by students by 3.5 points, by lecturers – by 3.6 points. The comparison of assessments of different university canteens showed that in buildings, located far from the university administrative building, all aspects of canteen operation were assessed lower.

**Fig. 1.** Assessment of the Kemerovo State University canteen operation, which is visited most often by students and lecturers, by three aspects and upon the whole (by a 5-point scale, where 1 point is very badly, and so on increasingly, 5 points - very good) (points).

Comparison of indicators of students’ attitude to canteens operation depending on their prosperity level showed an interesting interdependence - those, who have greater prosperity, gave more loyal assessments to the all items of canteens operation and those, whose financial possibilities are more limited, assessed it more critically. Based on the foregoing, we can state that students are not satisfied with canteens operation because of high prices and food quality, and this causes eating of less healthful food. In general, the opinions of students strongly enough coincided with the views of the teaching staff, which further confirms the reliability of the results.

According to the data of another all-university research, conducted in spring, 2014 (sociological research covered 963 students from freshman to senior of all faculties), less than a half of respondents (42%) could afford a healthy nutrition; almost as many as those who have to economise for it (41%). There are quite a few of those (12%), who "have to economise harmfully for nutrition, because money is not enough at all" (12%). According to the data of comparative analysis, students, having a lower income and living in a dormitory, were in a more vulnerable position.

Thus, a sociological substantiation, built on the data secondary analysis, demonstrated the importance of a more careful attention to students’ nutrition arrangement. In this case it is necessary to study the respective experience of different countries, Russian regions and municipal formations, in particular, the experience of nutrition arrangement in comprehensive schools, which has been gained during the Russian reform in school catering service.

In most countries of the world with advanced state welfare activities, systems of pupils' centralised catering service are provided, where state subsidy is up to 80% of the diet price. Parents are also involved in school catering service financing; the method of multi-way financing is implemented. In the context of students, such systems are practiced in the frameworks of general nutrition programs.

In the USA (Food and Nutrition Service. URL: http://www.fns.usda.gov/programs-and-services) healthy children nutrition is implemented due to the current special programs. Thus, the National School Lunch Program is applied to children up to 18 years and covers more than 31 million Americans every day. Under this program school dinners shall comply with the specially designed nutrition standards, which presuppose a certain number of calories, an increased availability of fruits, vegetables and whole-grain products.

School Breakfast Program presupposes that breakfasts shall be included in nutrition regime. The program presupposes measures, motivating and encouraging pupils and their families to use school breakfasts.

Special Milk Program is intended for institutions that do not take part in the above-mentioned nutrition programs. Under this program, children may get milk.
for free or buy it at a reduced price (depending on the type of institution and program).

Under the Child and Adult Care Food Program, the standards of rational nutrition are developed. Most of its participants are preschool children who may get a balanced two-meal nutrition. The right to use this program depends on the poverty status of the district or on incomes.

Financial support for nutrition programs is implemented by the United States Department of Agriculture through a compensation for cash and product expenditures, as well as through financial aid to states to cover administrative costs, associated with the programs. Programs control in state institutions and schools is implemented by states individually, and in private schools and non-governmental institutions they act through special Food and nutrition services.

30.5 million pupils are provided with breakfasts and dinners as a result. Multi-way financing is implemented: each school, participating in the programs, receives federal subsidies directly on the school account or on the account of the district administration, to which it relates; from the nearest agricultural products suppliers schools also receive different food packages in the line of the Department of Agriculture in the amount of 20.75 dollars per dinner per pupil; from parents, who do not have any exemptions, a school receives from 15% to 90% of the pupils' nutrition cost. Totally, under all the programs approximately 12 billion dollars are appropriated in the USA for free nutrition.

In Great Britain (Children’s Food Trust. URL: http://www.childrensfoodtrust.org.uk/childrens-food-trust/schools/) systems of centralised catering service have the old-established tradition: in 1906 recommendations for municipal authorities were adopted for provision of free nutrition for pupils.

To the beginning of 1970s the country developed the available centralized nutrition system, which covered the majority of students, and for students from poor families it was free of charge. Since Margaret Thatcher has come to power in 1979, the program was phased out because it was considered costly and bureaucratic.

After school catering service had been criticised by the famous chief cook James Oliver, in 2005 extra-departmental state body was founded under the UK Department of education and training - School Food Trust. The Trust created the biggest national network of healthy culinary clubs for children and families with the support of a grant from the state and commercial organisations. Nowadays, the Trust is a registered philanthropy organization and a special advisor to the government on the issues of school catering service, children nutrition and the skills, associated with it. The main task is to ensure that all children have a balanced diet, cooking skills and education which will help to fully realize their potential. Cooking clubs activity covers 1.7 million people. Nearly all (92%) use their new skills at home, 58% of participants point out that they have a healthy diet due to the fact that they have learned to cook. Another big project of the Trust is training centres School FEAST Network (School Food Excellence And Skills Training Network). Under this project cooks of school canteens may improve their qualification to the 2nd level in accordance with the national standards. It is supposed that cooks of higher qualification will be able to provide better nutrition quality in children institutions.

School nutrition Service in Finland (Finnish Free School Meals are a central part of the food culture. URL: http://www.elo-saatio.fi/finnish-free-school-meals) provides daily free nutrition for approximately 830000 pupils from 7 to 19 years old.

The history of free nutrition is associated with the adoption in 1943 of the law under which municipalities were obliged to provide free breakfasts for pupils. Nutrition complex consists of traditional Finnish products and includes main hot course, vegetables, bread, fat-free or low-fat milk and water.

Special diets are being developed, which include increased content of vegetables, fruits and whole-grain products. According to the recommendations, in educational institutions the number of sweets and sweet carbonated drinks shall be minimised; thus, vending machines and school kiosks shall offer healthy and nutritious products.

Municipal and school training programs define the central nutrition principles. Municipalities allocate resources for school catering service and are responsible for the program implementation. Implementation, quality and efficiency are the components of general education assessment. Pupils have a possibility to take active part in the assessment at obligatory attention to their feedback.

On the average, the price of products for cooking one dinner is 0.6-0.8 euros. Food is more expensive for those who need diet food. The amount of financing of school nutrition is 354 240 euros. Average price of one school dinner is about 2.64 euros. Applying multi-way financing, state obliges municipal budgets by law to provide pupils with free nutrition, which is due to tax revenues to local budgets and revenues from religious communities. Commercial operators and Social-purpose Products Management deal with pupils’ nutrition arrangement. Parents are excluded from the number of school catering service investors.

In some countries there are special programs of nutrition for students. Thus, in Canadian Toronto there is a functioning program Student Nutritiion (Student Nutrition Program. URL: http://www1.toronto.ca/wps/portal/contentonly?vgnextoid=ecad946d1d592410VgnVCM10000071d6089RCRD), which covers 160 thousand people daily. Under the program, students get breakfast, lunch and dinner. The founders of this program claim its following tasks: provision of nutrients and energy, creation of healthy food habits, prevention of obesity. The municipality of Toronto allocates grants annually to school/student communities which arrange healthy nutrition for students in educational organisations. However, this financing covers only a small part of total expenditures for the program. The greatest part of program financing comes from parental contributions and local fundraising.
For example, the US Department of Agriculture introduced an electronic debit card instead of meal coupons. Traditionally, meal coupons were offered for working poor and single parents, most working young people older than 18 years old, studying at a college or other university, do not have the right to receive benefits of the supplemental nutrition assistance program (SNAP), but under the certain conditions, for example, presence of dependants, terms of benefits provision are softened (Supplemental Nutrition Assistance Program (SNAP). URL: http://www.fns.usda.gov/snap/students).

In Russia the experience of nutrition programs implementation is realised meanwhile in the system of school catering service. However, nowadays, the project of the federal law on social nutrition is being actively discussed and drafted. At the present time, in the Russian Federation social nutrition is provided for the population groups on the basis of the federal law “Ob osnovakh sotsial'nogo obsluzhivaniya grazhdan v Rossiyskoy Federatsii” [On principles of social service for citizens in the Russian Federation], No. 442-FZ dated as of 28.12.2013 (Federal law dated as of 28 December, 2013 No. 442-FZ “Ob osnovakh sotsial'nogo obsluzhivaniya grazhdan v Rossiyskoy Federatsii” [On principles of social service for citizens in the Russian Federation] URL: http://base.garant.ru/70552648/#help). This law specifies the population groups, provided with social service, as well as indicates that provision of social service recipients with free hot meals is included in the list of social services. The law on social nutrition operates in Saint-Petersburg from 2008 and is being elaborated in Moscow, Tver etc. Experimental sites for implementation of this system are operating in some regions. According to the law, socio-economic system should be created, associated with servicing of various categories of consumers. Social nutrition is a possibility to provide nutrition at the budget expense for certain categories of citizens to ensure social guarantees, stipulated by the current legislation. Under this proposal the following nutrition systems by the consumer contingent are pointed out: working, student, school, children, therapeutical nutrition and the one in military educational institutions. They have a common designated purpose but differ in the significance level and the degree of population coverage.

Norms of catering service at universities will be included in a separate section in this bill. So, we can assume that the catering service system at universities will be built on the model of school catering service.

Under the implementation of the Federal program “Modernizatsiya shkol'nogo pitania” [School Catering Service Modernisation], the main aim of which is “complex modernisation of the system of school catering service: provision of 100% of pupils with balanced hot meals in accordance with physiological needs of children and hygiene requirements for catering service”, in municipal formations, beginning with 2008 combines of school catering service have been founded in the form of state unitary enterprise and municipal autonomous institutions for the possibility to arrange centralised production of high-quality products under the single production cycle regardless the personnel qualification level of educational institutions food units.

Thus, for Kemerovo schools the municipal autonomous institution (MAI) “Shkol'noe pitanie” [School Catering Service] produces meals for school canteens (School Catering Service. – URL: http://sray-min.p/l), which was founded by the decision of the Kemerovo Municipal Property Management Committee (No. 639 dated as of 09.04.2008 in accordance with the Kemerovo Mayor Decree No. 1356 dated as of 04.04.2008). Under the implementation of the project “Shkol'noe pitanie” [School Catering Service] from 2008 till 2011 nearly all school food units were modernised (only a few units, which meet the modern requirements, remained without modifications): facilities were reconstructed, equipment and furniture in dining halls were replaced, cyclic menu was designed, innovative approach to cooking treatment was implemented, the system of quality and nutrition control of pupils was designed.

To involve the maximum number of pupils in rational nutrition, the Kemerovo administration compensates the fifth part of all enterprise expenditures and this allows to ensure the price of school meals lower than the market one. Moreover, the innovations affected also the payment procedure for school catering service, which is made with the use of billing system, which allows parents and form-masters to solve the issues of nutrition process management at the modern level (payment, expenditures control, nutrition orders forming etc.). The module “Shkol'noe pitanie” [School Catering Service] is a part of the service “Elektronnuyj zhurnal” [Electronic Journal].

MAI “Shkol'noe pitanie” [School Catering Service] practices production of 20-day menu which is formed in complexes and is regularly renewed (taking into account the season). Meals are not repeated in the menu. The used products have a high nutrition value; they are treated with a low-impact technology, aimed at minimising the loss of nutrient substances during cooking. Careful attention is obligatory paid to the quality and safety of raw materials and finished products. MAI “Shkol'noe pitanie” [School Catering Service] Process Department together with Rospotrebnadzor [Federal Service on Surveillance for Consumer Rights Protection and Human Well-being] and Inspection Committee in an educational institution are responsible for control in this area. The following is conducted under the production control: laboratory control of raw materials and finished products quality; field inspections of food units by the specialists of Rospotrebnadzor [Federal Service on Surveillance for Consumer Rights Protection and Human Well-being] and instrumental examination of microclimate, light and noise. Raw materials and finished products quality are controlled by the specialists of enterprise process department and by the enterprise sanitary inspector.

In conclusion of review of the practice of pupils and students catering service and its regulatory support, it should be mentioned that nowadays, the Common Standard of student nutrition is being developed in Russia, initiated by the Russian Student Community
CONCLUSIONS

The analysis of the foreign and Russian practice of students and pupils catering service shows that principal improvement of student nutrition is possible only at circumspect comprehensive approach to its arrangement. The issue of student rational nutrition should have a status of the state program and there is a hope that the Russian state moves in the appropriate direction. However, taking into account the current economic situation, in the near future one can face the barriers on the way to the centralised solution of the problem of students nutrition. In these circumstances, the regional and municipal bodies could take this issue under control. In this case, a management difficulty, associated with university departmental subordination, occurs, but when you consider that universities and institutions in remote areas train personnel, primarily for the economy of the respective regions, then this problem can and should be solved.

It seems that the task of centrilised catering service arrangement at universities may be resolved easier in relatively small municipal formations, on the territory of which there are several (up to ten) educational institutions of higher education. Kemerovo is precisely such a municipal formation. The important factor, which should affect the municipal complex arrangement positively and which provides students with healthy nutrition, is the presence in the city of the specialised university - the Kemerovo State Institute of Food Industry (University), which may be a scientific-methodological centre on the alleged production complex.

The new production complex should supply qualitative finished food, products and semi-finished products for cooking meals directly at universities, as well as train personnel of educational organisations canteens and control the nutrition quality in them. The alleged products should have optimum quality-price ratio, i.e. they should guarantee a high quality of products and services in combination with price availability. Enterprise should be equipped with the modern equipment, have experienced personnel, professional dietitians should conduct formulations, there should be a continuous quality control over both the incoming products and semi-finished products and over the outcomes products. Thus, the structure of production complex on centrilised production foodstuffs for universities in the city should include: scientific research laboratory for generation of scientifically grounded menu; laboratory control for conduction of incoming inspection and control over the outcomes products, including measures for production control in canteens and buffets of educational organisations; meat shop (meat and poultry dissection, production of coarse- and fine-lump semi-finished products, forming of semi-finished products; candy production, producing a wide range of small-piece baked products; culinary production of salads and culinary products; logistics centre, where common warehouses are located and raw materials are packaged for universities/buildings; kitchen factory for production of breakfasts and lunches for serveries.

The foundation of scientific research complex for provision of students of the city with nutrition, including dietary one, may solve the following social and economic problems: to improve students nutrition quality and, consequently, improve their health; unload universities from non-specific activities; provide cost efficiency and ability to manage public catering: create new workplaces, including high-technology ones; buy products from local producers more actively; develop and implement special programs (for students with different diseases, for vulnerable students, for students living in dormitories etc.) and others. In any case, centrilised student catering service arrangement in municipal formation is a subject, requiring careful attention and management decisions.

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compliance with manuscript requirements. In discussing the results, it is mandatory to set forth a sound conclusion on the novelty of the content submitted for publication.

The articles are accepted in the text editor Microsoft Word using the font Times New Roman, font size 10. The manuscript should contain no less than 7–10 pages, typewritten with the single line spacing and having 2-cm-wide margins on all sides. The article size also includes an abstract, tables, figures, and references.

Each article sent to the journal should be structured as described below.

1. In the top left corner of the first page there is the UDC (Universal Decimal Classification) index.
2. Title. It is necessary to give a short, informative, and precise name of the work.
3. Name(s) and initials of the author(s).
4. The name(s) and affiliation to the institution(s) where the research was carried out, the country, city, zip code, e-mail address and phone (of the author).
5. Abstract. An abstract of 180–250 words should reflect fully both the main results and the novelty of the article.
6. Key words (no more than 9).
7*. Introduction. A brief review of the problem dealt with in the study and the validation of the approach taken are presented. References are given in square brackets and numbered (beginning with no. 1) in the order of their appearance in the article. With several references appearing in sequence, they should be placed in the chronological order. The aim of the study should be clearly formulated.
8*. Objects and methods of research.
   – For describing experimental work, the section should contain a full description of the object of the study, consecutive steps of the experiment, equipment, and reagents. The original names of equipment and reagents should be specified, and the manufacturer’s name (company, country) should be given in parentheses. If a method is not widely known or is considerably modified, please provide a brief description in addition to the reference;
   – For presenting theoretical research, the section should contain the tasks, approximations and assumptions, conclusions, and solutions of basic equations. The section should not be overloaded with intermediate data and the description of well-known methods (such as numerical methods of solving equations) unless the authors have introduced some novelty into them.
9*. Results and discussion.
   – The section should provide a concise description of experimental and/or theoretical data. Rather than repeating the data of tables and graphs, the text should seek to reveal the principles detected. The past indefinite tense in describing the results is recommended. The discussion should not reiterate the results. This section should be completed with a major conclusion that answers the question specified in the introductory part of the article.

* In case of surveys, these sections do not need to be entitled. The contents may present an analytical survey of the problem chosen and give the widest reflection of the existing points of view and data related to the theme. The article should necessarily contain the grounds for the problem’s timeliness and the author's conclusion on the prospects of the approaches given for the solution of the problem analyzed.

Each table is to consist of no less than three columns and have a number and a title. The journal publishes black-and-white photographs and diagrams.

Recommendations for typewriting formulae: mathematical equations forming a separate line should be printed in the MathType formula editor as a whole. It is not allowed to combine a table, a text, and an inserted frame within the same unit. For the equations printed in the MathType, it is necessary to keep to the standard style of symbols and indices, as well as their size and placing. Forced manual changing of individual symbols and formula elements is not allowable!

10. References.

They should be formatted according to the common standard. The list of papers is typed on a separate page in the order of their appearance in the text. All authors of each cited paper are indicated. If there is an English version of the paper, it is necessary to refer to it, indicating the DOI.

For cited journal articles, the names and initials of all authors, the name of the article, the name of the journal (for foreign journals, it is necessary to keep to the CASSI), year, volume, number, and page are indicated.

For cited books, the names and initials of the author(s), the name of the book, publisher, year, volume, number, part, chapter, and page are given.

For cited collections of articles, abstracts; conferences, symposiums, etc., the author(s), the name of the work, the name of the collections (conference, symposium), city (place of holding), publisher, year, volume, number, and the paper's first page are indicated.

References to web resources are to be given in the body of the text.

There should be no references to publications that are not readily available. These include institutional regulations, state standards, technical requirements, unpublished works, proceedings of conferences, extended abstracts of dissertation, and dissertations.

The absence of references to foreign authors and to the cited papers of 2–3 year novelty reduces the chances of a manuscript's publication. The references should reflect the actual impact of representatives of different countries on the investigation of a particular problem.

11. The following information should be sent in English: the title of the article, the authors' initials and surnames, an abstract, key words, the name of the institution (with the mailing address, telephone number, and e-mail).
Documents may be presented in the Russian, English, and German languages.

The following papers are sent to the editorial board.
1. A soft version of the article typewritten in MS Word. The file of the article should be entitled by the first author’s surname, e.g., PetrovGP.doc. The data file must only contain a single document.
2. A printed copy of the article identical to its soft version. In case of discrepancies between them, the editor gives preferences to the electronic version of the manuscript.
3. Personal information: the full names of all authors, the place and the mailing address of their places of work, the subdivision and position, the academic degree and rank, the honorary degree, the telephone number, the personal mailing and electronic addresses, the date of birth, and a reference to the author’s scientific profile.

The author to contact is indicated by an asterisk. The file should be entitled with the first author's name, e.g., PetrovGP_Anketa.doc.

4. A cover letter to the editor-in-chief from the responsible organization with the conclusion about the work urgency and recommendations for its publication, carrying the date, reference number, and the head’s signature.
5. An external review on the article according to the sample, the reviewer's signature being authenticated by the corresponding HR subdivision.
6. A standard copyright agreement. The manuscript’s electronic version may be e-mailed to the editorial office at fjournal@mail.ru.

**RECOMMENDATIONS**

For the article file use the format *.doc. Do not use Russian letters and spaces in the file's name.

The article file is to be identical to the printed original submitted to the editorial board.

The article's textual file is to include the title of the article, an abstract, a structured text, references, a separate sheet of captions for the diagrams, and tables (each on a separate sheet). Structural chemical formulae are placed in the body of text.

The articles are accepted in the text editor Microsoft Word using the font Times New Roman for texts, Symbol for Greek letters, and MathematicalPi2 for handwritten and gothic symbols. The standard font size is 14.

For tables, use Word (Table – Add Table) or MS Excel.

**Recommendations for typewriting formulae**

Mathematical equations forming a separate line should be typed in the MathType formula editor as a whole.

It is not allowed to combine a table, a text, and an inserted frame within the same unit. For the equations printed in the MathType, it is necessary to keep to the standard style of symbols and indices, their size and placing. Forced manual changing of individual symbols and formula elements is not allowable!

**Dimensions**

They are separated from the figure by a space (100 kPa, 77 K, 10.34(2) Å), except for degrees, percent, and permille: 90°, 20°C, 50%, 10‰. Fraction dimensions: 38 J/mol, 50 μl/2.

For complex dimensions, it is allowed to use both negative degrees and parentheses (J/mol-1 K-1), [J/(mol K)] or [J/(mol K)-1], if it makes reading easier. The main requirement is the unified manner of writing dimensions.

While enumerating and giving numerical spaces, the dimension is set for the last number (18–20 J/mol), with the exception of angular degrees.

For Celsius degrees: 5°C, not 5°. Angular degrees are not omitted: 5°–10°, not 5–10°.

Dimensions for variables are written with a comma (E, kJ/mol); for logarithms, in square brackets without a comma: ln t [min].

**Spaces between words**

References to diagrams and tables are typed with spaces (Fig. 1, Table 2).

Inverted commas and brackets are not separated by spaces from the included words: (at 300 K), (a); not (at 300 K ), ( a ).

There should be a space between the № or § sign: (№ 1; § 5.65), but no space in numbers with letters: (IVd; 1.3.14a; Fig. 1d).

In geographical names, there is a space after the period: p. Енисей, г. Новосибирск.

**References to cited works**

Initials are put after authors’ and editors’ names and are not separated by spaces: Иванов, А.А., Петров, В.Б.

The year, volume, number, etc. are separated from one another and from the figures by spaces: 1992, vol. 29, no. 2, pp. 213.

To refer to the issue number of both Russian and foreign journal, use the № sign. In the titles, the word journal is shortened for Journ.

Before the year of issue after the publisher's name or city (if no publisher), there is a comma.

**Graphic material**

The journal publishes black-and-white illustrative material.

While making graphic files, keep to the following recommendations:

**Vector pattern.** schemes, and diagrams are preferably to be presented in the format of the application in which they were carried out or in EPS. For other illustrations, it is preferable to use TIFF and JPEG formats, optimum resolving capacity being 300 dpi.

**Photographs** should be submitted in 2 variants.

The first one should correspond to the paper-based original, with marks and inscriptions; the second one should not contain any text, captions, etc. The advisable file formats are TIFF and JPEG, the optimum resolving capacity being 300 dpi. The gray color shade is allowed from 9 to 93%.

All illustrations are to be saved as separate files in the folder. Every file contains one picture.